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H/D exchange studies of methane activation mechanisms in heterogeneous catalysis

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The development of technologies for the efficient conversion of methane and other light hydrocarbons is becoming vital to the chemical industry. The main technologies for methane conversion are based on solid and liquid catalysts such as metals, oxides and oxide-supported metals. Methane is a highly stable molecule, and the analysis of the catalytic activity of materials with respect to the C-H bond cleavage in methane is of paramount importance for the development of novel methane conversion catalysts. One of the most promising methods for studying methane activation over a catalyst is H/D isotope exchange between the gas and condensed phases. The method provides reliable in situ information on the cleavage of chemical bonds in molecules and allows researchers to elucidate the elementary steps of catalytic methane activation and the stable intermediates involved in the activation process. This paper focuses on the critical analysis of H/D isotope exchange studies of the methane activation mechanism over various metals, oxides, composites, and other catalysts, from the earlier studies to the recent advances in the field. The existing theoretical and experimental approaches to study the H/D exchange between methane and a catalyst are discussed in the paper. A critical analysis of the structure-composition-catalytic activity relationships of the catalysts with respect to methane activation is provided.

keywords: H/D exchange, methane activation, heterogeneous catalysis, metals, oxides, composites, supported catalysts, superacids

1. Introduction

For more than 70 years, the issues of hydrocarbon conversion have attracted the attention of researchers all over the world [1]. The last decades have been marked by the increased interest of the chemical industry in the application of light hydrocarbon conversion technologies for hydrogen energy production [2–5]. Solid oxide electrochemical devices (SOEDs), especially proton ceramic electrochemical devices (PCEDs) are the most promising types of devices for hydrogen energy production. SOEDs and PCEDs are capable of converting the energy of a redox reaction between an oxidant (air) and a hydrogen-containing fuel to produce electricity and high value-added chemical products.

Various hydrocarbons can be used as fuel for SOEDs and PCEDs [3, 6–8]. However, methane can be considered as the most promising hydrocarbon, mainly due to its accessibility in nature. The conversion of methane can be used to obtain many important compounds such as ethane, ethylene, acetylene, benzene, molecular hydrogen, syngas, and methanol, which can be further applied to energy production and organic synthesis [9–13]. However, methane is known to be one of the most stable hydrocarbons, with the energy of C–H bond cleavage being about 435 kJ · mol^{-1}. Thus, the application of catalysts is essential for methane conversion. The basic reactions of catalytic methane conversion with their enthalpies and reaction temperatures are summarised in Table 1.

To be applied as a catalyst for the methane conversion, a material has to meet strict requirements such as high thermal and chemical stability in methane

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Table 1 – Enthalpies and temperature conditions for processes of the methane catalytic conversion [9–13].

	ΔH^0_{298}, kJ · mol⁻¹	Temperature range, °C
$2CH_4 \longrightarrow H_2 + C_2H_4$	202	600–1000
$6CH_4 \longrightarrow 9H_2 + C_6H_6$	532	700–1000
$CH_4 + H_2O \longrightarrow CO + H_2$	206	800–1000
$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$	247	600–1000
$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2$	−36	≥ 700
$2CH_4 + O_2 \longrightarrow C_2H_4 + 2H_2O$	−281	≥ 700
$2CH_4 + O_2 \longrightarrow C_2H_6 + 2H_2O$	−177	≥ 700

containing atmospheres, high tolerance to cocking formation, high catalytic activity related to C–H bond cleavage and, in the case of electrocatalysis and PCED applications, high electrical conductivity.

These requirements have caused the extensive studies of various catalysts for methane conversion beginning from the first half of the 20th century and to the present [14, 15]. To date, hundreds and thousands of papers have been devoted to the study of different types of methane conversion catalysts. The three main groups of the catalysts are metals, oxides, and metal-oxides [10, 16]. The study of catalysts is known to be a complicated issue, which includes the clarification of the mechanism of the methane activation over the catalysts and the finding of the key factors governing the mechanism. Various experimental techniques have been developed to solve this issue.

One of these techniques is H/D isotope exchange, which allows the *in situ* study of the kinetics of the mass transfer of hydrogen isotopes between the gas phase and a catalyst. This technique can help the researcher to find: the elementary steps of methane activation; the active centres of a catalyst surface involved in methane activation; and the stable methane adsorbed species involved in the methane activation process. Up-to-date, several reviews [17–19] have been written on the H/D isotope exchange in catalysis. However, a complete and comprehensive analysis of the papers dealing with the H/D isotope exchange between methane and catalysts with regards to hydrogen energy production, taking into account the different approaches to data description, has not been written yet.

Thus, the aim of this paper is to provide a critical and comprehensive analysis of the studies devoted to the H/D isotope exchange between methane and methane conversion catalysts, from the earliest papers to the most advanced studies, taking into account the different experimental and theoretical approaches used by the authors.

2. H/D exchange: theory and experiment

2.1. Design of H/D exchange experiments

The phenomena of H/D exchange in molecular hydrogen and hydrocarbons have been known since the beginning of the 20th century [14, 20–22]. However, it was only around the 1950s that the development of gas-phase analysis techniques became good enough to apply the methods to study the kinetics of the H/D exchange between methane in the gas phase and a catalyst i.e. to analyse the change in H and D isotope concentrations [23, 24]. In this subsection we briefly discuss the most common experimental techniques that have been used to date to analyse the kinetics of the H/D exchange.

The major characteristics of the experimental techniques most commonly used for the analysis of the kinetics of the H/D exchange between methane and catalysts are presented in Table 2. The first method allowed to analyse the change in hydrogen isotope concentration in time is infrared spectroscopy. infrared spectroscopy provides the information about the vibrational frequencies of chemical bonds in adsorbed gas molecules or a solid. In the 1930s Morikava and co-workers [14, 22] were the first to study the H/D exchange between CH_4 and D_2 over a Ni surface. Using the difference in vibrational frequencies of C–H and C–D bonds (2030 cm⁻¹ and 2250 cm⁻¹), the authors managed to identify the change in the intensity of C–D bond over time which was the first and direct evidence of the H/D exchange between methane and D_2. The most remarkable studies devoted to the H/D exchange between methane and a catalyst with the application of infrared spectroscopy were conducted in the 1990s by G.J. Kramer and co-workers [25], where the authors used infrared spectroscopy for the analysis of the kinetics of the H/D exchange between methane and zeolites. The authors [25] analysed the change in the intensities of O–H and O–D bonds over time and calculated the apparent activation energies of the exchange. The main advantage of infrared

Table 2 – Experimental techniques for the studying of the kinetics of the H/D exchange between methane and a catalyst.

Experimental technique	Measured values	Advantages	Disadvantages
Infrared Spectroscopy	The intensities of resonance frequencies related to the vibration of O–H / O–D and C–H / C–D bonds	The possibility of calculating the change in the deuterium mole fraction in methane and the different active centres of a solid	The inability to calculate mole fractions related to different methane isotopologues; the requirements for methane preadsorption on a catalyst
Mass spectrometry	Ionic currents related to different molecular and fragment ions of methane isotopologues	The possibility of calculating mole fractions related to methane isotopologues and other gas phase components. The variety of experimental approaches for the experiments (IE GPE, SSITKA, PIE)	The inability to calculate the hydrogen isotopic composition in a solid
^{1}H Nuclear magnetic resonance spectroscopy	The intensities of resonance frequencies related to the change in local neighbourhood of H atoms in methane and a solid	The possibility of the simultaneously calculating the change in the isotopic composition of methane and a solid; the possibility of calculating mole fractions related to methane isotopologues	Relatively low temperature range of the technique application; the requirements for methane preadsorption on a catalyst

spectroscopy in the application for H/D exchange studies is its applicability for the analysis of hydrogen isotope distribution in solid materials, which can show catalytically active and inert H-containing chemical bonds in a solid. However, the method shows the change in the isotopic composition in separate bonds, whereas in the case of the isotope analysis of the gas phase it is essential to measure the concentration of the different types of isotopically labelled molecules (isotopologues) such as CH_4, CH_3D, CH_2D_2, CHD_3 and CD_4, which is beyond the capabilities of infrared spectroscopy.

The development of mass spectrometry allowed the researchers to measure *in situ* the time dependences of the concentrations of methane isotopologues in the gas phase and to analyse the kinetics of the H/D exchange. The first studies in this field were carried out by Wright and Taylor [23] in 1946 and to date, most of the H/D exchange studies have been carried out with the mass spectrometry analysis of the isotopic composition of the gas phase. This analysis is based on the measurements of ionic currents related to the charged fragments of different masses. The mass-spectra for each pure methane isotopologue are described with the unique combination of fragment ions with different intensity of each fragment [26–28]. And the mass spectra of the mixture of methane isotopologues can be considered as the mixture of their individual spectra [24, 29]. One of the main problems of mass spectrometry in the case of the H/D exchange study is the calculation of the mole fractions of the methane isotopologues from the mass spectra of the mixture of the methane isotopologues composed of overlapping spectra of individual isotopologues.

So far, three main approaches have been proposed to solve the problem of the calculating the mole fractions of the methane isotopologues: the calculation from the intensities of the molecular ions under conditions of low ionisation voltage (12–14 eV), when the intensities of the fragment ions are negligibly low [24]; from the intensities of molecular ions with the subsequent subtraction of the intensities related to the fragment ions using the mean mass spectra of CH_4 and suggesting the equality of the probabilities C–H and C–D bond cleavage during methane fragmentation in a mass spectrometer [30]; the application of an artificial neural network, which was preliminarily trained on a data set containing the different mixtures of methane isotopologues [31]. All three approaches have their advantages and disadvantages: the first approach allows the direct calculation of isotopologue mole fractions from mass spectra. However, it has problems in measuring concentrations related to by-products such as H_2O due to the overlap of molecular ion signals related to H_2O and CH_2D_2. The second approach is free from this problem due to the differences in the mass spectra of H_2O and CH_2D_2 at higher ionisation voltages.

However, the application of the mean spectra of CH_4 and the assumption of the equality of C–H and C–D bond cleavage during methane fragmentation results in lower accuracy of the calculated concentrations. The third approach allows the accurate calculation of mole fractions related to any molecule in the gas phase. However, it requires the training procedure to be replaced each time the setting of a mass spectrometer is changed.

Nevertheless, the flexibility of mass spectrometry has led to the development of different types of isotope exchange techniques i.e. the isotope exchange with the gas phase equilibration (IE GPE), the steady state isotope transitient kinetic analysis (SSITKA), and pulsed isotope exchange (PIE) [24, 30–33]. In IE GPE method a sample is equilibrated in a closed reactor chamber under relatively low pressure of a gas with a given isotopic composition, followed by the exchange with an isotopically labelled gas such as D_2 and CD_4. In SSITKA the sample is equilibrated in a gas-flow reactor under a flow of a gas-carrier mixture with a natural isotopic composition, followed by the change of the gas-carrier mixture with an isotopically labelled gas. In PIE method the sample is equilibrated in a gas-flow reactor under a flow of a gas-carrier mixture with a natural isotopic composition as in the SSITKA case, while the H/D exchange experiments are carried out by the injecting pulses of an isotopically labelled gas. The main disadvantage of mass spectrometry is its inapplicability for the analysis of the isotopic composition of solids. To overcome this problem some authors have attempted to analyse the kinetics of the H/D exchange using both infrared spectroscopy and mass spectrometry [30, 34].

The last and most recent method to analyse the kinetics of the H/D exchange between methane in the gas phase and a catalyst is proton paramagnetic resonance ^{1}H-NMR. This method is based on the adsorption of electromagnetic radiation in the frequency range of about 4–900 MHz. The main feature of ^{1}H-NMR that makes it applicable to the H/D exchange is the change in the resonant frequency of H (chemical shift) depending on the local neighbouring atoms in its vicinity. Walspuger and co-workers [35] studied the H/D exchange between CH_4 and DSO_3F SbF_5 with using ^{1}H-NMR and showed the applicability of ^{1}H-NMR to the measurements of chemical shifts related to different methane isotopologues. Stepanov et al. [36] demonstrated the applicability of ^{1}H-NMR for studying the H/D exchange between methane and zeolite catalysts with the measurement of chemical shifts related to methane isotopologues and zeolite OH groups, which makes ^{1}H-NMR the only method that allows *in situ* study of the isotopic composition in both methane and a catalyst. The main disadvantages of this method are the relatively low temperatures of the H/D exchange experiments (below 400 °C) and the difficulties of methane-catalyst sample preparation for the application in the ^{1}H-NMR spectrometer.

Up to date, the most widespread method of the H/D exchange kinetics studies is mass spectrometry, which is caused by its flexibility and accessibility, while the infrared spectroscopy is mostly used as an additional *ex situ* technique for the studying of the isotopic composition of the solid. The ^{1}H-NMR technique is only in the beginning of its development for the analysis of the kinetics of the H/D exchange. So far, only several groups have applied this method, mostly to study zeolite catalysts. However, ^{1}H-NMR has great potential for development due to its ability to *in situ* study the change in isotopic composition both in the gas phase and in catalysts.

The high accessibility of mass spectrometry has resulted in the development of various theoretical approaches for the analysis of the H/D exchange kinetics between the gas and solid phases. In the next section, we discuss these approaches in brief.

2.2. Theoretical approaches

It is known that the H/D exchange between methane and a catalyst occurs by the reversibly breaking of −H / −D bonds in methane and a hydrogen-containing catalyst. The driving force of the H/D exchange is the change in Gibs free energy. Due to the close values of the enthalpies of isotopolgues formation, the enthalpy of the H/D exchange reactions has close-to-zero values and the main factor governing the change in the Gibs free energy is an entropy factor. The dominance of the entropy factor in H/D exchange reactions causes the statistical, i.e. binomial, distribution of hydrogen isotopes in methane at isotopic equilibrium observed by Kembal in a CH_4–D_2 exchange over metals [17]. Conventionally, all H/D exchange reactions are classified in two main groups i.e. *exchange reactions* are the reactions between a hydrocarbon and a deuterium-containing agent e.g. D_2 or a D-containing solid, and *equilibration reactions* are the reactions of the H/D exchange between the species of the same substance without the participation of D-containing agent. In general, exchange reactions represent the H/D exchange between chemically different species here, and further they will be referred to as *heterogeneous exchange reactions*, while *equilibration reactions* will be referred to as *homogeneous exchange reactions*. Both terms are widely accepted in the field of ^{18}O / ^{16}O isotope exchange between O_2 and a solid [37–39] and, in our opinion, reflect the nature of these reactions more accurately. The detailed description of these two types of the H/D exchange reactions and the fundamental basis of the H/D exchange deserves a full, comprehensive review in itself, and here we restrict ourselves to a brief description of the most general approaches proposed by some authors to describe the kinetics of the heterogeneous and homogeneous H/D exchange reactions.

The first approach that many authors independently used is conventional formal chemical kinetics, which considers the fitting of the time dependences of mole fractions related to different methane isotopologues with a first-order exponential equation (1) containing one kinetic parameter, i.e., the rate constant of isotopologue formation or disappearance [34]:

$$\ln\frac{x_i-x_i^{\infty}}{x_i^{0}-x_i^{\infty}} = \pm k\tau, \tag{1}$$

where x_i is the mole fraction of the methane isotopologue with *i* deuterium atoms; x_i^0 and x_i^∞ are the mole fractions at zero and infinite time; *k* is the rate constant of the reactions and τ is time. This approach was conventionally used to analyse the homogeneous H/D exchange reaction of methane over oxide catalysts [34, 40]. It allows rough estimation of the reaction rate but does not give any information about methane adsorbed species and intermediates on a catalyst surface during the exchange. The conclusion about the type of adsorbed species was made on the basis of the type of methane isotopologue formed during the exchange e.g. if the author observes the formation of CD_3H and CDH_3 in the mixture of CH_4 and CD_4, then the adsorbed species are methyl radicals [34].

The second and most widespread approach was proposed by Kemball in 1951 in his paper [24] and further developed in his and Anderson's works [41, 42]. During the study of the heterogeneous H/D exchange in the mixture of $CH_4 + D_2$ over Ni Kemball found the formation of CH_3D and CD_4 as the major products of H/D exchange at the beginning of the experiment. Kemball associated the formation of CH_3D and CD_4 with two types of heterogeneous H/D exchange reactions, which further laid the basis of Kemball-Anderson approach.

The Kemball-Anderson approach is based on the consideration of the heterogeneous H/D exchange in mixtures of D_2 (~ 100 at. % D enrichment) and CH_4 (~ 0 at. % D enrichment) over a solid catalyst with two types of heterogeneous H/D exchange reactions: *stepwise exchange* which represents the subsequent exchange of one H atom in a hydrocarbon with D at the beginning of the experiments (2) and *multiple exchange* which represents the exchange of ≥ 2 H atoms in methane at the beginning of the experiments (3):

$$C_mH_n+D_a \overset{r_\mathrm{I}}{\rightleftharpoons} H_a+C_mH_{n-1}D, \tag{2}$$

$$C_mH_n+\sigma\, D_a \overset{r_\mathrm{II}}{\rightleftharpoons} \sigma\, H_a+\sum_{i=1}^{n}\frac{x_i}{\sum_{i=1}^{n}x_i}C_mH_{n-i}D_{i+1}, \tag{3}$$

where D_a and H_a are adsorbed deuterium and protium atoms formed by the dissociative adsorption of D_2 and CH_4 on a catalyst surface; C_mH_n is a hydrocarbon molecule with *m* carbon atoms and *n* hydrogen atoms; r_I and r_II are the rates of stepwise and multiple exchange reactions; σ is a parameter called multiplicity. The multiplicity corresponds to the mean number of hydrogen atoms exchanged between the hydrocarbon and the catalyst at the initial time (in the case of methane $1 \le \sigma \le 4$). The simulated time dependences of mole fractions related to methane isotopologues for *stepwise* and *multiple exchange* reactions are presented in Figure 1.

In this approach σ is the key parameter that describes the mechanism of the H/D exchange. In the case of *stepwise exchange* $\sigma = 1$, while in the case of *multiple exchange* $1 < \sigma \le 4$. The two ways were suggested for the calculation of σ parameter: from the distribution of hydrogen isotopes in methane at the beginning of H/D exchange experiments (~ 10 minutes) according to the equation (4); from the ratio (5) using the hydrogen heterogeneous exchange rate (r_H) expressed as $r_\varphi = 4r_H$ which is calculated from McKay exponential kinetics [43] of the time dependences of the mean deuterium fraction in methane (δ) (6) and the rate of CH_4 disappearance k_0 calculated from (1):

$$\sum_{i=1}^{n}\frac{ix_i}{\sum_{i=1}^{n}x_i} = \sigma, \tag{4}$$

$$\sigma = \frac{r_\varphi}{k} = \frac{r_I + hr_{II}}{r_I + r_{II}}, \tag{5}$$

$$\ln\frac{\varphi-\varphi^{\infty}}{\varphi^{0}-\varphi^{\infty}} = -r_\varphi(1+\lambda)\tau, \tag{6}$$

where $n = 4$ for methane; *h* is the mean number of hydrogen atoms exchanged between methane and the catalyst, leading to the formation of methane isotopologues with $i \ge 1$ deuterium atoms; $\varphi = \sum_{i=0}^{n} ix_i = n\delta$; φ^0 and φ^∞ are the values of φ at zero and infinite time; λ is the ratio between the number of hydrogen atoms in methane and molecular hydrogen. It should be noted that the nature of *stepwise* and *multiple exchange* processes is arguable [18, 24, 44], the detailed description of the uncertainty related to the nature of these reactions is discussed in Subsection 3.1.

The main advantage of the Kemball-Anderson approach is its simplicity. It allows the description of heterogeneous H/D exchange kinetics between any hydrocarbons and solid catalysts without solving complex systems of differential equations proposed by other

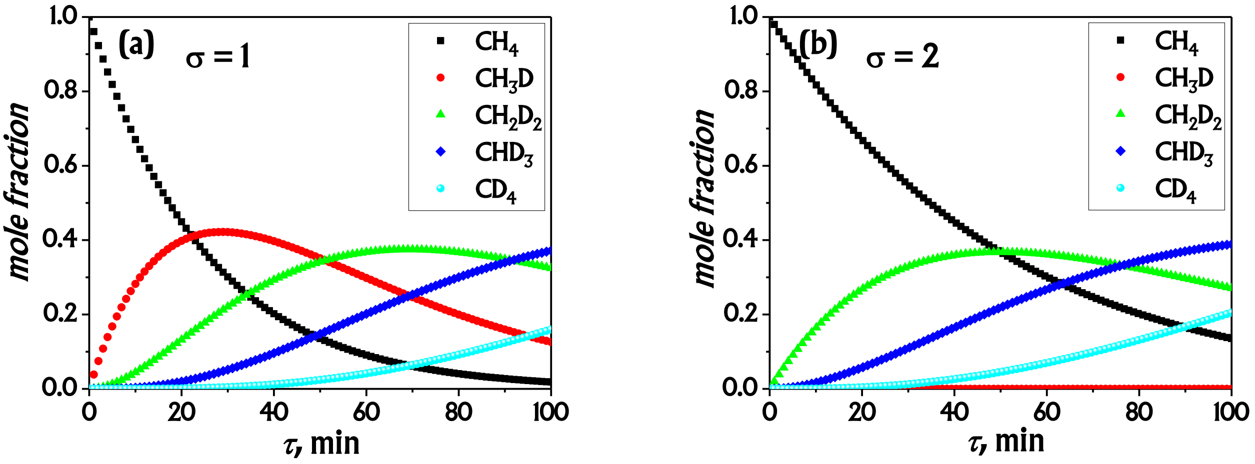


Figure 1 Simulated time dependences of mole fractions related to methane isotopologues for (a) *stepwise* and (b) *multiple exchange* reactions in the Kemball-Anderson approach.

authors [44, 45]. The discrimination of the methane activation mechanism can be performed with only two independent exponential kinetic equations (1) and (6). This advantage has made the Kemball-Anderson approach the most widespread approach in the field of the H/D exchange kinetic studies. However, the approach has many disadvantages such as the neglect of the homogeneous H/D exchange in methane; the restriction of the initial conditions of the H/D exchange, i.e. only the application of D_2 (~ 100 at. % D enrichment) and CH_4 (~ 0 at. % D enrichment) mixtures is acceptable; the total inapplicability of the approach for the analysis of the homogeneous H/D exchange reactions; the insufficiency of two kinetic parameters for the description of complicated multi-step mechanisms.

The third approach was developed in the Boreskov's school of catalysis by Shestov and Muzykantov in the 1980–1990^s [46–49] on the basis of Muzykantov's theory of isotope exchange [50–53]. In the Shestov-Muzykantov approach, the H/D exchange between methane and a solid catalyst was considered as the reversible dissociative adsorption of methane with the formation of negligibly small numbers of H_3, H_2, and H species on the surface, which govern the exchange process. The elementary reaction for this dissociation can be written as follows:

$$CH_4 + j(\ \ )_S \rightleftharpoons j(H)_S + \nu_1 H + \nu_2 H_2 + \nu_3 H_3 + C, \qquad (7)$$

where $(\ \ )_S$ and $(H)_S$ are free and occupied adsorption centres on the solid catalyst; ν_1-ν_3 and j are stoichiometric coefficients. Using different sets of stoichiometric coefficients Shestov defined eleven types of methane dissociative adsorption expressed by the matrix of stoichiometric coefficients (8). The first four strings in (8) represent the types of homogeneous H/D exchange. The simulated time dependences for these four types of dissociation are depicted in Figure 2 (a).

$$\begin{pmatrix} 0 & 4 & 0 & 0 \\ 0 & 2 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 2 & 0 \\ 1 & 3 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 2 & 2 & 0 & 0 \\ 2 & 0 & 2 & 0 \\ 3 & 1 & 0 & 0 \\ 4 & 0 & 0 & 0 \end{pmatrix} \qquad (8)$$

The Shestov-Muzykantov approach considers every mechanism of the H/D exchange as a combination of eleven types of methane dissociation and the total rate of the H/D exchange between methane and the solid catalyst can be represented as the sum of the rates for the respective types of methane dissociation.

The main advantage of the Shestov-Muzykantov approach is that it can be applied for the description of any possible multistep mechanism of H/D exchange between methane and any solid catalyst. The authors managed to unite the homogeneous and heterogeneous H/D exchange reactions in one complete system of differential equations which in general allows a researcher to analyse the kinetics of H/D exchange between methane

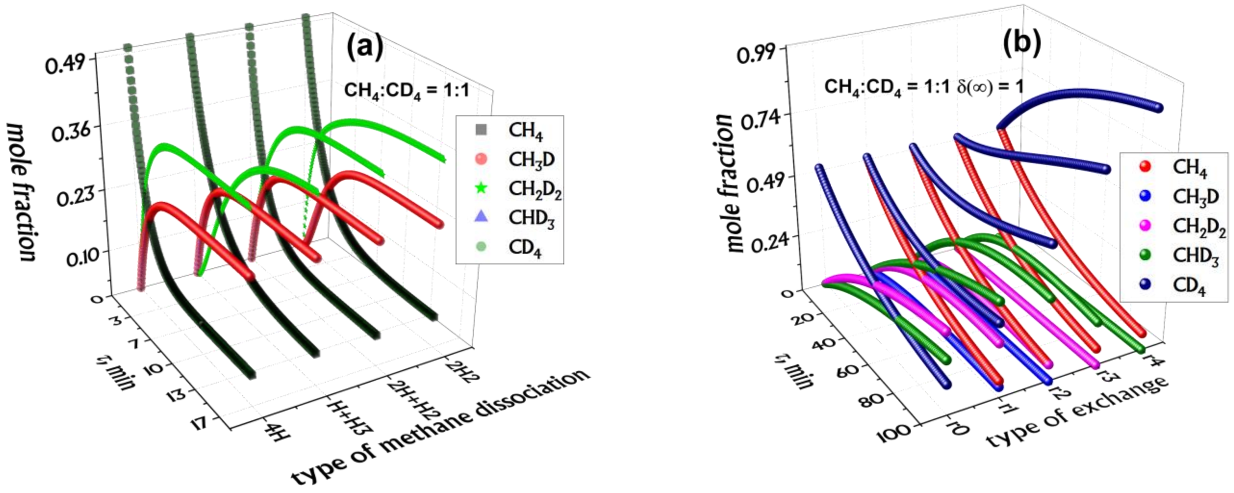


Figure 2 Simulated time dependences of mole fractions related to methane isotopologues for (a) four types of methane dissociation in Shestov-Muzikantov approach, (b) the five types of exchange in the five types of exchange theory.

and a catalyst under a variety of conditions. However, the analytical solutions of the isotope-kinetic differential equations are complex and have not presented by the author in his publications [46–49]. The assumptions of the existence of the negligible, unmeasurable amounts of H, H$_2$, and H$_3$ species on a catalyst surface in the absence of $(H_2)_S$ and $(H_3)_S$ complexes were not justified by any studies.

The last and most recent approach was proposed in our paper [31] in 2020 and called the five types of exchange theory. The theory was based on widely accepted three types of exchange theory developed independently by Klier and Muzykantov [37, 38] for oxygen isotope exchange between O$_2$ and oxides. According to the five types of exchange theory the process of the H/D exchange between methane and a catalyst can be described by the five types of hydrogen isotopes redistribution: the exchange of zero, one, two, three and four hydrogen atoms in an elementary act of the H/D exchange. The reactions of the five types of exchange for methane isotopologues can be written in general form as follows:

$$CH_{4-i}D_i+4X_g \overset{r_0}{\rightleftharpoons} (4-i)D_g+iD_g+CX_4, \tag{9}$$

$$CH_{4-i}D_i+3X_g+X_S \overset{r_1}{\rightleftharpoons} (4-i)H_g+(i-1)D_g+D_S+CX_4, \tag{10}$$

$$CH_{4-i}D_i+3X_g+X_S \overset{r_1}{\rightleftharpoons} (3-i)H_g+iD_g+H_S+CX_4, \tag{11}$$

$$CH_{4-i}D_i+2X_g+2X_S \overset{r_2}{\rightleftharpoons} (2-i)H_g+iD_g+2H_S+CX_4, \tag{12}$$

$$CH_{4-i}D_i+2X_g+2X_S \overset{r_2}{\rightleftharpoons} (4-i)H_g+(i-2)D_g+2D_S+CX_4, \tag{13}$$

$$CH_{4-i}D_i+2X_g+2X_S \overset{r_2}{\rightleftharpoons} (3-i)H_g+(i-1)D_g+H_S+D_S+CX_4 \tag{14}$$

$$CH_{4-i}D_i+3X_s+X_g \overset{r_3}{\rightleftharpoons} (4-i)H_s+(i-1)D_s+D_g+CX_4, \tag{15}$$

$$CH_{4-i}D_i+3X_s+X_g \overset{r_3}{\rightleftharpoons} (3-i)H_s+iD_s+H_g+CX_4, \tag{16}$$

$$CH_{4-i}D_i+4X_s \overset{r_4}{\rightleftharpoons} (4-i)D_s+iD_s+CX_4, \tag{17}$$

where X is any hydrogen isotope D or H; the subscripts g and s represent methane in the gas and solid phases; r_0, r_1, r_2, r_3 and r_4 are the rates of the five types of exchange. The total rate of the H/D exchange in terms of the five types of exchange theory is the sum of the rates of the five types of exchange and the hydrogen heterogeneous exchange rate is expressed as $r_H = \sum_{i=0}^{4} \frac{i \cdot r_i}{4}$. Any mechanism of the H/D exchange between methane and a catalyst in the five types of exchange theory can be expressed through the fractions of the five types of exchange, similar to the Shestov-Muzykantov approach [54].

The main advantage of the approach is its mechanism-free nature, i.e. the reactions (9)–(17) make no assumptions about the types of adsorbed species involved in the exchange. Thus, the five types of exchange theory can be used for the clarification of methane and other four-labelled-atom substances activation mechanisms over a catalyst [54]. Similar to the Shestov-Muzykantov approach the five types of exchange theory allows a researcher to simultaneously analyse both the homogeneous and heterogeneous H/D exchange reactions under a variety of experimental conditions. However, the analytical solution of the system of differential isotope-chemical equations system is still has a complicated form. According to the view of reactions (9)–(17) the approach is restricted with the types of the H/D exchange reactions that consider all four methane atoms to be equally and independently exchangeable.

To summarize, four general approaches for the description of the H/D exchange between methane and a catalyst exist in the literature. The formal chemical kinetics and Kemball-Anderson approaches can be considered as the most widespread but at the same time the least accurate, while the Shestov-Muzykantov and five types of exchange approaches allow an accurate description of the methane activation mechanism but have the most complicated system of differential equations.

The existence of four independent approaches makes the comparative analysis of data obtained by different authors difficult. In order to compare the results obtained by different authors, let us choose the parameters that can be considered as general for all approaches. These parameters are the total rate of the H/D exchange r ($r \approx k$ in the Kemball-Anderson and formal chemical kinetics approaches); the hydrogen heterogeneous exchange rate r_H which is the same for all considered approaches on account of the same form of the exponential kinetic equation of the mean deuterium fraction in methane (6); and the parameter σ that in the case of the Shestov-Muzykantov and five types of exchange theory approaches can be calculated directly from the rates of the eleven types of methane dissociation and the five types of H/D exchange using the equation:

$$\sigma = \frac{4r_H}{\sum_{k=5}^{11} r_k} = \frac{4r_H}{\sum_{i=1}^{4} r_i}. \tag{18}$$

The comparison of the results obtained using the Shestov-Muzykantov and five types of exchange theory approaches can be additionally performed if we equate the rate of r_0 type with the rate of the first type of methane dissociation (line 1 in matrix (8)), the rate of the r_1 type with the rate of the fifth type of methane dissociation (line 5 in matrix (8)), the rate of the r_2 type with the rate of the eighth type of methane dissociation (line 8 in matrix (8)), the rate of the r_3 type with the rate of the tenth type of methane dissociation (line 10 in matrix (8)) and the rate of the r_4 type with the rate of the eleventh type of methane dissociation (line 11 in matrix (8)). Let us now critically discuss the existed papers related to the H/D exchange between methane and various catalysts from the beginning of the 20th century until the most recent studies.

3. Methane conversion catalysts

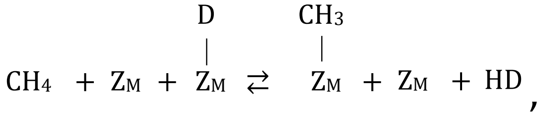
3.1. Metals

Metals are the most popular and widespread type of materials for the catalyst of methane and other hydrocarbons activation. Even today, the application of metals in heterogeneous catalysis plays a key role in the development of novel materials for hydrocarbon conversion [55]. In terms of the H/D exchange, metals were the first catalysts studied using the H/D exchange in methane-containing atmospheres.

In general, experiments on the H/D exchange between methane and metals were carried out in mixtures of CH_4 and D_2 with the excess partial pressure of D_2 at the temperatures below 400 °C [14, 22–24, 41]. The choice of these conditions is likely to be connected with the requirements of the exclusion of methane decomposition on metals in conditions of low molecular hydrogen pressures and high temperatures.

To date, the most commonly studied metals using the H/D exchange method are Ni, Pt, Pd, Ru, Rh, W and alloys based on Pt, Pr, Ru, Rh. The first studies devoted to the H/D exchange between methane and metals were carried out by Morikava at al. [14, 22] in the 1930s. The authors investigated the H/D exchange between methane and Ni in the mixtures of CH_4–CD_4, CH_4–D_2 and CD_4–H_2. It was found that the rate of the H/D exchange in the mixture of CH_4–CD_4 was higher than in the mixture of CH_4–D_2 in 15.7 times at 138 °C, in 3.5 times at 184 °C and in 3.9 times at 218 °C. For the first time, the authors proposed the mechanism of methane dissociative adsorption with the formation of CH_3 species on H-free adsorbed centres over the Ni surface. Wright and Taylor [23] also proposed methane dissociative adsorption as the mechanism of methane activation on Ni surface. However, the authors considered the coexistence of CH_3, CH_2, CH and C species on the Ni surface. Kemball [24] found that the kinetics of the H/D exchange between methane and Ni can be described by coexistence of *stepwise* and *multiple exchange* (see Section 2.2), with the dominance of *multiple exchange*. The same was found for Rh, Pt, Pd and W in his next paper [41]. Other results were obtained by McKee and Norton [56–59] who found that in the case of Pt and Pd catalysts *stepwise exchange* was the dominant process with σ parameter values to be 1.3–1.7 for Pt and 1.0–1.7 for Pd. Similar results for Pt were obtained by Guczi [60]. The results of the authors [56] for Rh and Ru revealed the dominance of *multiple exchange* with σ parameter values to be 1.0–3.6 for Rh and 2.5–3.1 for Ru. Anderson and Macdonald [61] analysed the influence of the surface structure of Ni evaporated films ({100}, {111} and random film orientations) on the methane activation mechanism and found that the values of σ did not depend on the surface structure of the Ni films.

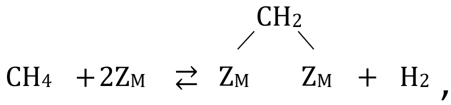
The first attempts to clarify the elementary steps of the methane activation mechanism were made by Kemball [24, 41]. The author found that D_2 reaction order during the H/D exchange is negative and varied in the range from −0.5 to −0.1, while the reaction order for methane varied from 0.3 to 1.0. To explain the negative reaction order for D_2, Kemball suggested that methane and molecular hydrogen compete for adsorption centres on the metal surface. Taking this competition into account, Kemball explained the *stepwise exchange* process as a one-step methane-molecular hydrogen dissociative adsorption reaction:



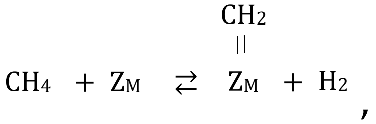
$$CH_4 + Z_M + \overset{D}{\overset{|}{Z_M}} \rightleftarrows \overset{CH_3}{\overset{|}{Z_M}} + Z_M + HD, \qquad (19)$$

where Z_M is a vacant adsorption centre on the metal surface. This one-step interpretation of the *stepwise exchange* seems to be arguable at least due to the simultaneous interaction of four species in one exchange step.

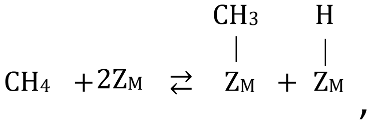
In order to explain the *multiple exchange* process, Kemball proposed four possible elementary reaction steps, i.e. the competitive dissociative adsorption of methane and molecular hydrogen with the formation of double bonded CH_2 species (20), (21) and the stepwise dissociation of methane to CH_3 and CH_2 species (22), (23):



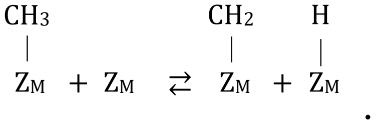
$$CH_4 + 2Z_M \rightleftarrows Z_M\overset{CH_2}{\diagup\;\diagdown}Z_M + H_2, \qquad (20)$$



$$CH_4 + Z_M \rightleftarrows \overset{CH_2}{\overset{||}{Z_M}} + H_2, \qquad (21)$$



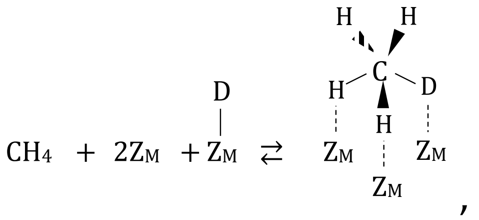
$$CH_4 + 2Z_M \rightleftarrows \overset{CH_3}{\overset{|}{Z_M}} + \overset{H}{\overset{|}{Z_M}}, \qquad (22)$$



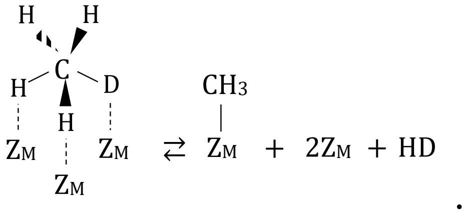
$$\overset{CH_3}{\overset{|}{Z_M}} + Z_M \rightleftarrows \overset{CH_2}{\overset{|}{Z_M}} + \overset{H}{\overset{|}{Z_M}}. \qquad (23)$$

The stepwise dissociation of methane over metals was also considered as the interpretation of *multiple exchange* by Miyahara [44] and McKee et al. [56–59]. Miyahara suggested that *multiple exchange* occurs as the result of the stepwise dissociative adsorption of methane with the formation of CH_3, CH_2 and CH species and the dissociative adsorption of molecular hydrogen over the metal surface. The rates of molecular hydrogen dissociative adsorption and CH_2 dissociation were assumed to be much faster than the rates of CH_4 and CH_3 dissociation.

Frennet [18] and Bolder at al. [45] suggested another possible interpretation of *stepwise* and *multiple exchange* processes. Frennet considered the formation of a six-atom three-centre activated complex (CH_5) of methane and hydrogen adatoms on the metal surface. This process can be represented schematically as follows:



(24)



(25)

Frennet supposed that reaction (24) corresponds to *stepwise exchange,* while reaction (25) corresponds to *multiple exchange.* McKee and Norton [57] supposed that both reactions (24) and (25) could be responsible for *stepwise exchange.* Bolder et al. [45] used their own mathematical approach and showed that both *stepwise* and *multiple exchange* can be described as a single process of the transition of methane to the activated state with the subsequent H/D exchange. In this case, *stepwise exchange* can be observed if the rate of methane deactivation is much higher than the rate of exchange, while *multiple exchange* is observed in the opposite case.

It should be noted that the interpretation of the *stepwise* and *multiple exchange* processes proposed by Frennet as well as Kembals interpretation are based on the atomicity of the hydrogen transition, i.e. the number of hydrogen atoms exchanged between methane molecules and metals in one elementary step. The atomicity of the hydrogen transition does not provide any information about the structure and the geometry of activated complexes or adsorbed species present on the metal surface. Frennet's suggestions about the mechanism of methane activation on the metal surface are based on *ab initio* studies [62, 63], that proved the stability of CH_5 species in the gas phase in vacuum and the studies of chlorine isotope exchange between CH_3Cl + HCl mixture and metals [64]. The usage of these studies to justify the existence of activated CH_5 complex on metal surface seems to be unreliable on account of the drastically different systems and conditions used in these papers. In our paper [65] we applied the five types of exchange theory to describe Kemball's data related to the H/D exchange between methane and Ni film in CH_4–D_2 mixtures. The results of the data fitting showed that *stepwise exchange* observed by Kemball corresponds to the pure n-type of the exchange (see Equations (10), (11) in Section 2.2) while *multiple exchange* corresponds to the combination of the n_3- and n_4-types of exchange (see Equations (15)–(17) in Section 2.2). The description of *stepwise exchange* in terms of a single kinetic parameter does not provide

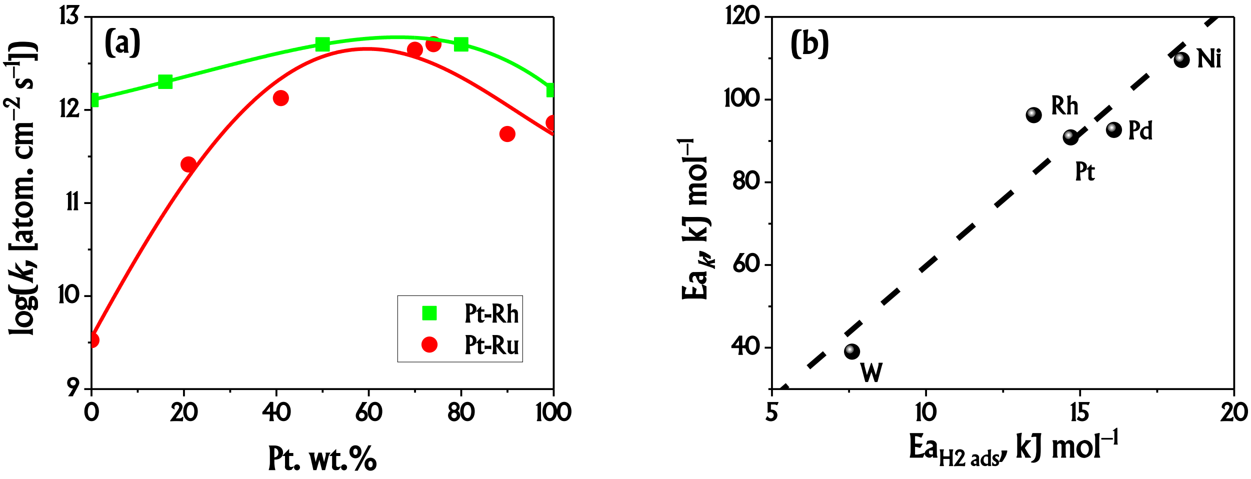


Figure 3 (a) Composition dependences of *k* for Pt-Rh [57] and Pt-Ru [56] alloys; (b) the dependence of the apparent activation energies for *k* calculated from Kemball's data [41] on the activation energies of H_2 adsorption taken from [67].

information about the type of intermediate species involved in the process, while the combination of the r_3- and r_4- types in the *multiple exchange* case supports the interpretation of Kemball [24, 41], Miyhara [44] and McKee et al. [56–59]. In papers [31, 54] we analysed different mechanisms of methane dissociative adsorption and H/D exchange and showed that the combination of the r_3 and r_4-types can be associated with fast stepwise dissociative adsorption of methane with the formation of CH species.

Thus, the nature of the species involved in *stepwise exchange* is still under discussion; the H/D exchange results obtained so far have not provided enough information to determine whether CH_3 or CH_5 species govern this process. This inconsistency is likely to be connected with the initial conditions of experiments, i.e. 0 at. % D enrichment of methane. Shestov in his PhD study [46] showed that at least in the homogeneous H/D exchange case when the D enrichment of methane > 0 at. % the formation of CH_3 species results in the appearance of the H + H_3 type of methane dissociation, while the formation of CH_5 species leads to the appearance of the 4H, 2H + H_2 and H + H_3 combination of methane dissociation types, which makes the steps related to CH_3 and CH_5 species formation kinetically distinct.

In the *multiple exchange* case, the stepwise methane dissociation is likely to be the most reasonable interpretation. However, the major species participated in *multiple exchange* are still under consideration. Kemball and Miyahara [24, 44] suggested that CH_2 species could be responsible for *multiple exchange*, while our recent results indicate CH species to be observable, whereas CH_3 and CH_2 to be kinetically "invisible". Let us now discuss the attempts made by some authors to describe the influence of metal composition on the methane activation mechanism.

The influence of metal composition on the methane activation mechanism was studied by McKee and et al. [56–59] in the mixtures of CH_4 and D_2 using the H/D exchange method. The authors studied the influence of alloy composition on the rate of the hydrogen heterogeneous exchange for the alloys Pt-Ru, Pt-Rh, Pt-Pd, Pd-Rh, Pd-Au. McKee and Norton found that the compositional dependences of the total rate of the H/D exchange (*k*) had maxima for Pt-Ru, Pt-Rh and Pd-Au alloys with 10–25 wt. % Ru, 30–40 wt. % Rh and 10 at. % Au (see Figure 3 (a)). The compositional dependences of *k* for Pt-Pd and Pd-Rh alloys showed bends at 50 wt. % Pd. The comparison of σ parameter values [57] for Pt-Ru, Pt-Rh, Pt-Pd, Pd-Rh showed the decrease in the metal radius (r_{Me}) in the series Pt > Pd > Rh > Ru and the increase in the mean number of unpaired *d* electrons in the series Pt = Pd < Rh < Ru the value of σ increased in the row Pt < Pd < Rh < Ru. The authors [57] suggested that the high mean number of unpaired electrons could be responsible for the high σ parameter values and the appearance of the maxima in the composition dependences of *k*, due to the stabilisation of the CH_2, CH and C species, which could have multiple Me–C bonds formed by means of these electrons.

We can suggest another possible explanation for the existence of maxima in the composition dependences of *k* for these alloys, related to the possible inhomogeneity of the alloys, that was not considered by McKee et al. In paper [66] Ananyev et al. have found maxima in the composition dependences of oxygen heterogeneous exchange rates for complex oxide composites based on Y-doped ZrO_2 (YSZ) and Sr-doped $LaMnO_3$ (LSM).

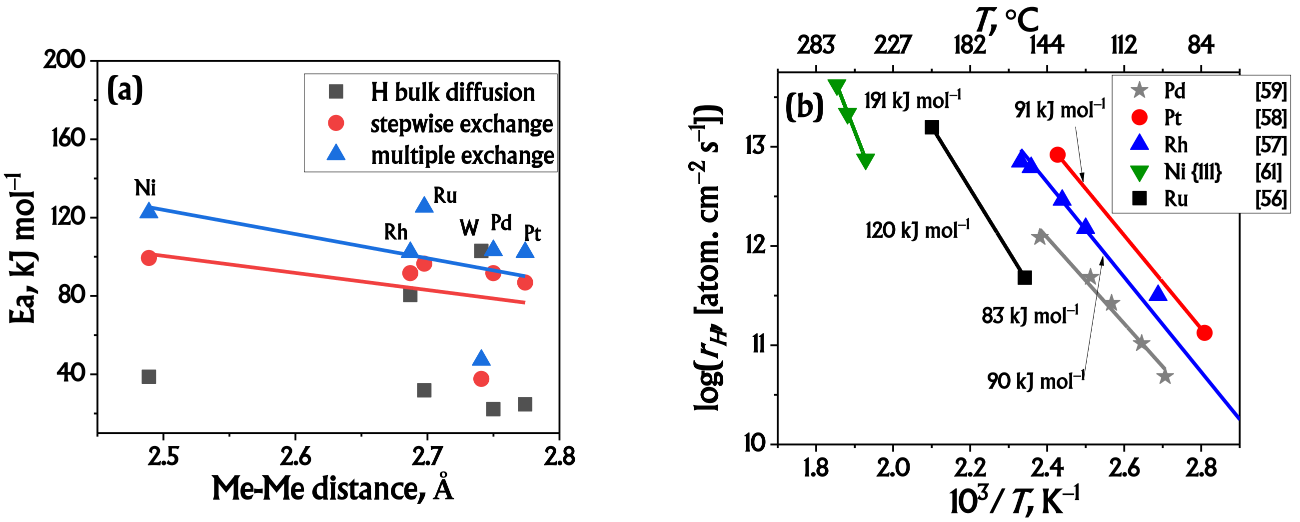


Figure 4 (a) The dependences of the apparent activation energies for hydrogen bulk diffusion, stepwise and multiple exchange taken from [41, 56, 70], on the Me-Me bond length for Ni, Ru, Rh, Pd, W and Pt; (b) the Arrhenius plot dependences of the hydrogen heterogeneous exchange rate taken from literature data [56–59, 61].

The appearance of the maxima was found to be associated with triple phase boundary (TPB) YSZ-O_2-LSM which created specific oxygen adsorption centres. Although these results were obtained for oxide systems, the similar behaviour is expected to be observed in the case of pronounced inhomogeneity of some alloys in the H/D exchange case. However, the effect of TPB on the H/D exchange between methane and metal alloys still needs to be clarified.

Interesting findings were made by McKee during the study the H/D exchange in the D_2–CH_4 mixture over Pd-Au alloys [59]. McKee found that the increase of Au at. % in Pd-Au alloys higher than 10 at. % results in a drastic decrease in *k* values, so that at 83.3 at. % of Au the author did not manage to find any exchange at 197 °C. McKee explains the effect of Au addition on *k* values with the inability of Au to dissociate D_2 in the mixture of CH_4 and D_2.

The results of McKee allow us to suggest that the effect of metal composition on methane activation is connected with the ability of metals to chemosorb hydrogen on their surface. Figure 3 (b) shows the dependence of the apparent activation barriers of *k*, calculated using Kemball's data [41], on the apparent activation barriers of H_2 chemosorption, taken from [67]. The figure shows the direct correlation between the apparent activation barriers of *k* and H_2 chemosorption. In Section 2.2 we have shown that *k* is a rough approximation of the total rate of the H/D exchange, which is equal to the methane dissociative adsorption rate [31, 54]. Thus, the correlation between the activation barriers of *k* and H_2 chemosorption can be considered as the correlation between the activation barriers of the methane dissociative adsorption and H_2 chemosorption. A possible explanation for the existence of this correlation can be found if we consider the reactions (20)–(25) discussed above. According to the reaction, the dissociative adsorption of methane is accompanied by the formation of chemosorbed H atoms. Thus, the metals that exhibit high activity with respect to H_2 chemisorption are likely to be highly active with respect to the methane activation. In this case, Hf and La can be considered as the most interesting metals for the study of the methane activation, as they have the lowest H_2 chemisorption activation barriers of 4.6 and 4.5 kJ · mol^{-1}, respectively [67].

Summarising the papers analysed in this section, one can conclude that the main attention of the researchers who studied the methane activation on metals using the H/D exchange method was focused on the types of methane adsorption species involved in the H/D exchange. It is well known that metals are able to absorb hydrogen [68, 69] by their structure. However, the influence of hydrogen diffusivity in the metal bulk on the kinetics of the H/D exchange between methane and metals was not even considered in these papers and still needs to be clarified. To understand the possible influence of hydrogen diffusivity, let us compare the activation barriers of hydrogen diffusion and the *stepwise* and *multiple exchange* reactions for metals.

The Me-Me bond-length dependences of the apparent activation barriers of hydrogen diffusion, *stepwise* and *multiple exchange* for metals are presented in Figure 4 (a). The figure shows that the apparent activation barriers for *stepwise* and *multiple exchange* are higher than the apparent activation barriers of hydrogen diffusion for all considered metals except W. The increase of Me-Me bond length leads to a decrease in the apparent activation barriers of both *stepwise* and *multiple exchange*, whereas the activation barriers of the hydrogen diffusion does not show a clear correlation with the Me-Me bond length. These results indicate that the hydrogen heterogeneous H/D exchange between methane and metals is likely to be governed by C–H bond cleavage, not by the hydrogen diffusion in the bulk of metals.

To conclude this section, let us make the comparative analysis of the metals with respect to their activity in methane activation, expressed in r_H. Figure 4 (b) shows Arrhenius-plot dependences of r_H calculated from literature data [56–59, 61] for Pt, Pd, Rh, Ru and Ni. According to the figure, Pt has the highest r_H values at temperatures below 150 °C. In terms of the application considered metals as components of electrochemical devices such as fuel cells, Pt is still the best metal for low-temperature applications such as proton-exchangeable membranes [71, 72]. However, at higher temperatures $\geq$ 300 °C Ni has a comparable value of r_H to Pt, which makes Ni a promising component for electrodes of proton ceramic electrochemical devices.

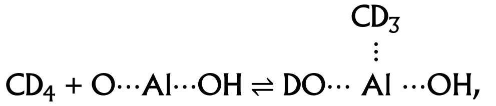
3.2. Oxides

Another type of materials for catalytic methane conversion is oxide materials. In contrast to metal catalysts, oxides are composed of at least two types of atoms, i.e. metal cations and oxygen anions that have different chemical and physical properties affecting methane activation. From a practical point of view, oxide catalysts are the main components of electrochemical devices, which can use methane as a fuel [9, 73, 74]. In catalysis, oxides are often used as supports for metals to stabilise their microstructure [9]; these metal-oxide catalysts will be discussed in the next section.

The majority of oxide materials cannot uptake hydrogen by their bulk, and, as a consequence, all the steps of methane activation over these oxides must take place in the adsorption layer of the materials. However, it is known [75–78] that some of oxide materials, such as yttria stabilized zirconia can exhibit hydrogen surface diffusion, which can influence the methane activation mechanism, while others can uptake hydrogen by their bulk forming OH bonds in the case of zeolites [26, 30] and ionic proton defects in the case of proton-conducting oxides [31, 54, 79]. In this section, we carry out the critical analysis of existing papers devoted to the H/D exchange between methane and oxide catalysts.

The kinetics of the H/D exchange between methane and oxides has been studied since the 1960th [80]. Among simple oxides, the most studied to date are γ-Al_2O_3, MgO, Cr_2O_3, CaO, SrO, BaO, La_2O_3, CeO_2, Pr_2O_3, Tb_2O_3, TiO_2, ZrO_2, ThO_2, ZnO, WO_3, La_2O_3, CeO_2, Pr_2O_3, Sm_2O_3, Gd_2O_3, Ho_2O_3, Tm_2O_3, Fe_3O_4, Ga_2O_3, MnO, Nd_2O_3, Pr_6O_{11}, V_2O_5, Yb_2O_3, SiO_2. In contrast to the studies devoted to metal catalysts (see Section 3.1), the papers related to oxides considered not only the heterogeneous H/D exchange in mixtures of CH_4 and D_2, but also the heterogeneous H/D exchange in pure methane and the homogeneous H/D exchange over the oxide surface.

One of the first papers dealing with simple oxides was the work of Larson and Hall [80]. The authors studied the heterogeneous and homogeneous H/D exchange between methane and γ-Al_2O_3. For the first time, the authors discussed the influence of metal cation charge on the mechanism of methane activation. Taking into account the studies of Perri et al. [81, 82], Larson and Hall suggested the mechanism of methane activation and the heterogeneous H/D exchange between surface hydroxyls on γ-Al_2O_3, which can be written as follows:



$$CD_4 + O\cdots Al\cdots OH \rightleftharpoons DO\cdots \overset{\overset{CD_3}{\vdots}}{Al}\cdots OH, \qquad (26)$$

where $O\cdots Al\cdots OH$ is an active adsorption centre on γ-Al_2O_3 surface. In reaction (26), the active adsorption centre of γ-Al_2O_3 is considered as a double acid-base site. In terms of Brønsted-Lowry acid-base theory [82, 83], oxygen ions O^{2-} in the adsorption layer behaved as a base that can take H atoms from the methane molecule, while HO^- can be considered as donors of H atoms that can recombine with CH_3 adsorbed species, forming CH_4. Quanzhi and Amenomiya [34] suggested a similar mechanism of methane activation over MgO and γ-Al_2O_3. Another interpretation of the methane activation mechanism over γ-Al_2O_3 was proposed by Engelhardt and Valyon in their paper [85]. The authors claimed that dehydroxylated γ-Al_2O_3 had no Brønsted acid sites and, as a consequence, should have Lewis dual acid-base sites $Al^{\delta+}O^{\delta-}$, where $Al^{\delta+}$ was considered as Lewis's acid interacting with $CH_3^{\delta-}$ and $O^{\delta-}$ as Lewis's base. Both interpretations of the activation mechanism of methane over simple oxides seem to be equivalent, since they deal with the same type of elementary step (26) and differ only in the charge state of the Al and O atoms, information about which cannot be extracted directly from the H/D exchange method. It should be noted that the acid-base description of the active centres involved in the methane activation can be considered as the most widespread approach in the case of oxide catalysts. For example, Bjørheim et al. [86] used a similar concept to describe the affinity of some oxides for proton, hydroxyl and oxygen ions. The papers devoted to zeolite and silica-alumina catalysts of hydrocarbon cracking also describe the active centres of the catalysts in terms of the Brønsted-Lowry acid-base theory.

Additional information on the methane activation over MgO and γ-Al_2O_3 was provided by Shestov in his PhD thesis [46]. The author found that the kinetics of the homogeneous H/D exchange in methane over MgO and γ-Al_2O_3 is described with two types of methane dissociation: the H_3 + H and H_2 + H, with 80 % and 20 % contribution to the total rate of the H/D exchange. Shestov interpreted the obtained data using the mechanism of stepwise methane dissociative adsorption accompanied by the formation of CH_3 and CH_2 adsorbed species over the oxides. Although Shestov did not make any conclusions about the active centres that can participate in the exchange process, his mechanism does not contradict the acid-base interpretation due to the ability of O···Al···O centres to adsorb two hydrogen atoms.

The study of the effect of the metal cations nature on the mechanism of the methane activation was carried out in papers [40, 87, 88]. Lacombe et al. [40] studied the homogeneous H/D exchange in methane over La_2O_3, CeO_2, Pr_2O_3, Sm_2O_3, Gd_2O_3, Ho_2O_3 и Tm_2O_3. The authors found that the increase of ionic radii of the metal cations led to an increase in the homogeneous H/D exchange rate. The homogeneous H/D exchange rates for La_2O_3, CeO_2, Pr_2O_3, Sm_2O_3 and Gd_2O_3, were found to reach maximum values in the temperature range 800–850 °C with a subsequent decrease. Lacombe et al. assumed that the partial reduction of the metals in the oxides can be responsible for the decrease in the rates of the homogeneous H/D exchange at higher temperatures. The maximum decrease of the homogeneous exchange rate was observed in the CeO_2 case at 800 °C where the conversion of CH_4 and CD_4 mixture in the mixture of CH_3D, CH_2D_2 and CHD_3 decreased from 95 % to 5 % in several minutes.

The studies of the heterogeneous H/D exchange between methane and oxides in mixtures of CH_4 and D_2 were carried out in papers [87, 88]. *Stepwise exchange* was found to be a dominant H/D exchange process for γ-Al_2O_3, MgO, CaO, SrO, BaO, La_2O_3, CeO_2, Pr_2O_3, Tb_2O_3, TiO_2, ZrO_2, ThO_2, ZnO, WO_3 [87, 89], while the competition between *stepwise* and *multiple exchange* was observed in the case of α-Cr_2O_3 [90]. Robirtson et al. [91] found a linear correlation between r_H and hydrocarbon acidity in γ-Al_2O_3 case, which supports the suggestion of Larson and Hall [80] and Engelhardt and Valyon [85] about the acid-base nature of γ-Al_2O_3 active centres.

Studies of isotope effects in the kinetics of the homogeneous and heterogeneous H/D exchange between methane and simple oxides were carried out by authors [80, 90]. Based on comparative analysis of the H/D exchange data obtained in the mixtures of CH_4 and CD_4; CD_4 and H_2; CH_4 and D_2, Larson and Hall [80] concluded that in the case of γ-Al_2O_3 the isotope effect of the heterogeneous and homogeneous H/D exchange was determined by the difference in the strengths of the C–H and C–D bonds (the rate of the H/D exchange was in 1.8 times higher in CH_4–D_2 mixture than in CD_4–H_2 mixture). The rate-determining step of the heterogeneous H/D exchange in the mixture of methane and molecular hydrogen was suggested to be connected with the breaking of C–D bonds, due to the studies of H_2/D_2 exchange over γ-Al_2O_3 that reveal unmeasurable fast homogeneous H/D exchange in molecular hydrogen at temperature –78 °C. Kalman and Guchzi [90] found kinetic isotope effects of the heterogeneous H/D exchange in mixtures of CD_4 – H_2 and CH_4 – D_2 over α-Cr_2O_3. The ratio of r_H(H) / r_H (D) varied in the range 1.5–2, and the increase in temperature up to 415 °C led to the disappearance of the isotope effect.

The main adsorbed species that governed the methane activation in the mixtures of CH_4 and D_2 over simple oxides were considered to be CH_3 [87, 90, 91]. Utiyama et al. [87] studied the heterogeneous H/D exchange in mixtures of CH_4 and D_2 over MgO, CaO, SrO, BaO, La_2O_3, CeO_2, Pr_2O_3, Tb_2O_3, TiO_2, ZrO_2, ThO_2, ZnO, WO_3 and suggested that the formation of CH_3 species over the series of oxides occurred during the removal of H^+ proton from CH_4 by the base centres of the oxides.

Hargreaves et al. [88] attempted to determine the effect of cation nature on the heterogeneous H/D exchange in mixtures of CH_4 and D_2 over the oxides Al_2O_3, CaO, CeO_2, Cr_2O_3, Fe_3O_4, Ga_2O_3, Gd_2O_3, La_2O_3, MgO, MnO, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, TiO_2, V_2O_5, Yb_2O_3, ZnO, ZrO_2. The authors found that the highest values of H/D exchange rates corresponded to Ga_2O_3 and ZnO, which was believed to be the result of partial reduction of the oxides. This explanation contradicts that of Lacombe et al. [40] who supposed the partial reduction of metal cations to be responsible for the decrease of H/D exchange rates. For the majority of oxides Hargreaves et al. did not manage to find the correlation between the ionic radii of the metal cations and r_H. However, in the case of rare-earth cations an increase in r_H was observed in the series La_2O_3, Nd_2O_3, Gd_2O_3, Yb_2O_3, which correlates with the results of Lacombe et al. [40] obtained for the homogeneous H/D exchange of methane in the series La_2O_3, CeO_2, Pr_2O_3, Sm_2O_3, Gd_2O_3, Ho_2O_3 and Tm_2O_3.

Summarizing the studies on simple oxide catalysts, one can conclude that in contrast to the studies on metal

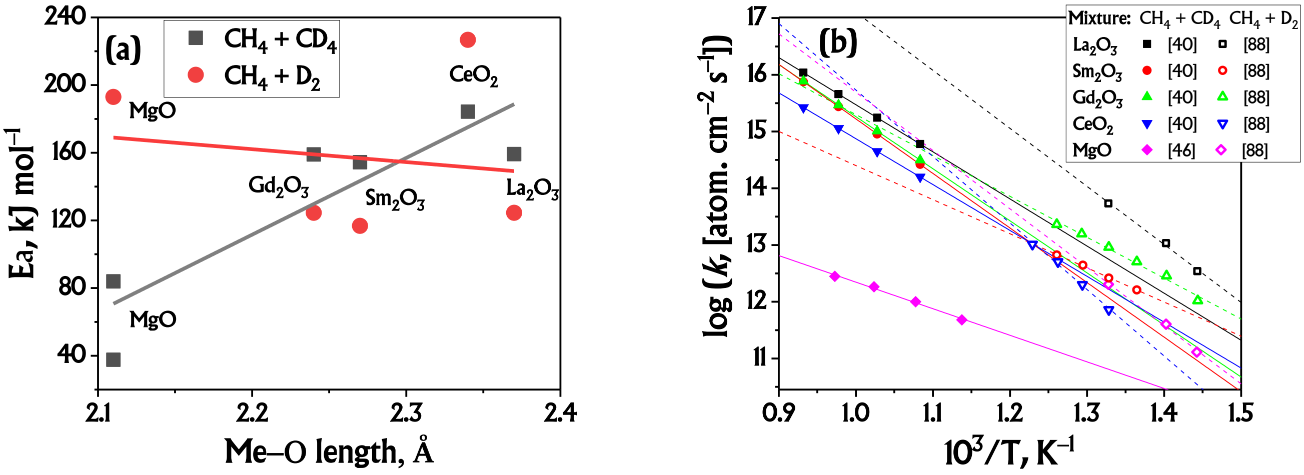


Figure 5 (a) The Me-O bond length dependences of the apparent activation energies of the heterogeneous and the homogeneous H/D exchange plot from literature data [40, 46, 88]; (b) the Arrhenius plot dependences of the heterogeneous H/D exchange rates taken from literature data [56–59, 61].

catalysts the authors of considered papers analysed not only the H/D exchange in mixtures of CH_4 and D_2, but also the H/D exchange in CH_4 and CD_4 mixtures, which allow us to estimate the activation barriers of C–H and C–D bond cleavage in the absence and the presence of molecular hydrogen. The bond length dependences of the activation barriers of the homogeneous H/D exchange in methane and the heterogeneous H/D exchange in CH_4 and D_2 mixtures for the studied oxides presented in Figure 5 (a). The figure shows that increasing the Me–O bond length leads to a slight decrease of the apparent activation barrier in the case of CH_4–D_2 mixtures, while a clear increase of the apparent activation barriers of the homogeneous H/D exchange with the Me–O bond length can be observed. The increase in the apparent activation barriers of the homogeneous H/D exchange with the length of Me–O bond can be clearly explained using the step (26) proposed by Larson and Hall [80] for γ-Al_2O_3, i.e. the increase in the length of Me–O bond increases the distance between the methane adsorption centres (Me cations) and the base centres that responsible for the removal of H^+ atoms from methane. The absence of such dependences for the heterogeneous H/D exchange in CH_4 and D_2 mixtures seems to be unexpected, especially if we take into account that the rate-determining step of the H/D exchange in the mixture of CH_4 and D_2 on the surface of simple oxides has to be C–H bond cleavage. The absence of the increase in the activation barrier of the heterogeneous H/D exchange in the mixtures of CH_4 and D_2 may be related to additional surface related processes. Methane and molecular hydrogen in the simple oxides have different adsorption centres: O^{2-} in molecular hydrogen case and Me^{z+} for methane adsorbed radicals and O^{2-} for hydrogen atoms in methane case. Thus, the surface diffusion of hydrogen adsorbed atoms between oxygen ions [75–79] and the molecular hydrogen desorption due to the reversible recombination of hydrogen adsorbed atoms can both promote the heterogeneous H/D exchange in the mixtures of methane and molecular hydrogen. These processes can be also responsible for the higher rate of the heterogeneous H/D exchange than the rate of the homogeneous H/D exchange in methane on the rare-earth oxides (see Figure 5 (b)).

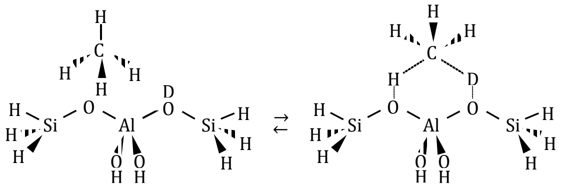
The comparison of the apparent activation barriers of the heterogeneous H/D exchange in mixtures of CH_4 and D_2 over simple oxides and metals (see Figures 4 (a) and 5 (a)) reveals that the barriers in the case of metals are lower at 60 kJ · mol^{-1} than in the case of oxides, which reveals that the acid-base sites of the methane dissociative adsorption are less energetically effective than the active centres of metals. However, in the metals case the same active centres are responsible for both the dissociative adsorption of methane and molecular hydrogen resulting in the competition between CH_4 and H_2 for the adsorption on each centre, whereas in the simple oxides case the centres are different which may result in the promotion of the methane activation by molecular hydrogen addition. This difference in the methane and molecular hydrogen adsorption centres makes simple oxides more preferable materials for the application as the components of fuel electrodes in electrochemical devices.

The studies of methane activation mechanisms over oxides that can uptake hydrogen from the gas phase were carried out in papers [25, 30, 36, 54, 80, 85, 92–100]. The majority of the studies have been devoted to silica-alumina catalysts, including zeolites.

The first papers on the H/D exchange between methane and silica-alumina catalysts appeared in the 1940^{s} [92]. The main feature of the oxides is the ability to chemosorb hydrogen from the gas phase with the formation of OH bonds. The two types of OH bonds considered in silica-alumina catalyst are silanol OH bonds related to O atoms bonded to Si atoms of the catalyst and bridge OH bonds related to O atoms bonded to Si and Al atoms [25, 30, 92, 98, 99].

Paravano et al. [92] found that the heterogeneous H/D exchange between methane and OH groups of the silica-alumina catalyst started at temperature 345 °C. Larson and Hall [80] studied the heterogeneous H/D exchange between CD_4 and the OH groups of the silica-alumina using the kinetic model, which was the direct equivalent of *stepwise exchange* of the Kemball-Anderson approach. The authors found only 2 % of the silica-alumina OH groups to be exchangeable.

To date, the most studied silica-alumina catalysts are zeolites with FAU-, MFI- and BEA- structure types [25, 30, 93, 96, 97]. In contrast to all the above-discussed papers, these studies focused on the investigation of the H/D exchange using *ab initio* methods [25, 93, 96, 97]. The calculations were carried out using clusters representing the active centres of zeolites, e.g. $H_3Si–OH–Al(OH)_2–O–SiH_3$, or $H_3Si–OH–AlH_2–O–SiH_3$. During the calculation, the authors determined the apparent activation barriers of the methane adsorption and geometric parameters of intermediate species involved in the H/D exchange. The authors of the papers [25, 93, 94, 96, 97] found that the methane activation over zeolites occurs through the formation of six-atom two-centred CH_5 complex, which is located on two oxygen atoms, with one oxygen atom behaving as the acid and the other as the base. The two O–D–C and O–H–C bonds of the zeolite-methane complex were considered to be responsible for the H/D exchange process. The exchange occurred when the O–D bond of O–D–C and the H–C bond of O–H–C simultaneously split up. The process can be represented with equations:


(27)

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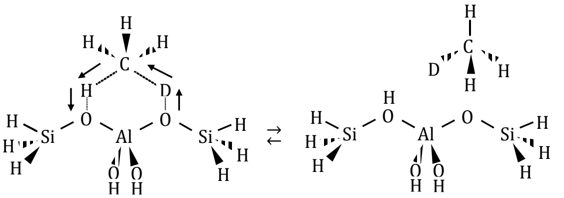
(28)

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The authors of the papers [25, 93, 94] found that the length of the O–H and the H–C bonds in O–H–C are 1.2 and 1.3 Å, respectively. Blazkovsky et al. [94] showed that the apparent activation energy of the heterogeneous H/D between methane and zeolites was 125 kJ · mol^{-1} in the case of reactions (27) and (28), and 343 kJ · mol^{-1} in the case of the methane dissociative adsorption with CH_3 formation. Volmer and Truong [96] obtained similar values of the activation energy for reactions (27) and (28) i.e 124 and 137 ± 5 kJ · mol^{-1}.

The experimental studies of the kinetics of the heterogeneous H/D exchange between methane and zeolites were carried out in the papers [25, 30, 85, 95]. Infrared spectroscopy was used by the authors to measure the change in the isotopic composition of the SiOH and SiOHAl groups of the catalyst. Kramer et al. [25] studied the kinetics of heterogeneous H/D exchange between CD_4 and two types of zeolites FAU (Si/Al = 10) and MFI (Si/Al = 13) in the temperature range 347–477 °C. The authors found that methane can interact only with SiOHAl groups of the zeolites. The possibility of the H/D exchange between the SiOH and SiOHAl groups was discussed. The authors also observed that the rate of the heterogeneous H/D exchange between methane and MFI-zeolite was higher than that related to FAU-zeolite.

Li et al. studied the heterogeneous H/D exchange between methane and ferrierite zeolite with Si/Al = 17 and found that the apparent activation energy of the exchange was 107 ± 16 kJ · mol^{-1}, which is similar to the values calculated with *ab initio* methods [95]. Schoofs et al. [30] studied the kinetics of the H/D exchange between methane and FAU and MFI zeolites with different Al/Si ratios in the temperature range 450–550 °C using both mass spectrometry (SSITKA method) and infrared spectroscopy techniques. The authors proposed a model described the kinetics of the H/D exchange between methane and the zeolites as *stepwise exchange* with 16 rate constants. The model takes into account the difference between the rates of direct and reverse reactions and isotope effects. It was found that the rates of the heterogeneous H/D exchange in the MFI zeolite case were 3 times higher than the rates in the FAU zeolite case. The apparent activation energies of the H/D exchange were found to depend on the Al/Si ratio and varied in the range of 120–150 kJ · mol^{-1}. The authors also made a conclusion that the SIOH groups are

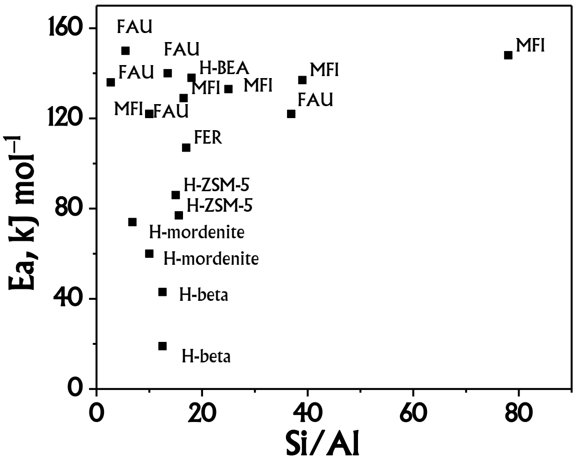

Figure 6 The dependences of the heterogeneous H/D exchange activation energies on the Si/Al ratio taken from papers [25, 30, 85, 95, 100].

only capable of the H/D exchanges with the SIOHAl groups. The mechanism of the H/D exchange was described by the authors [30] in terms of reactions (27) and (28). The existence of the isotope effect of the H/D exchange between methane and zeolites was first demonstrated by Schoofs et al. [30]. The authors claimed that the existence of the isotope effects of the H/D exchange (r_H(H)/r_H(D) = 1.6–1.7) indicates that the assumption of simultaneous breaking of the O–D bond of O–D–C and the H–C bond of O–H–C in the activated complex is incorrect. However, it should be taken into account that the authors of [30] described the H/D exchange between methane and the zeolites as *stepwise exchange* and neglected both *multiple exchange* and the homogeneous H/D exchange in methane, which makes their conclusions about the kinetics of the H/D exchange doubtful. Even the rough estimation of σ using the data presented in paper [30] after 30 minutes of experiment using eq. (4) gives the value of about 1.3, which indicates the contribution of *multiple exchange*.

Engelhardt and Valyon [85] studied the heterogeneous H/D exchange between CD_4 and H-mordenite, H-ZSM-5 and H-beta zeolites in comparison with γ-Al_2O_3 using PIE method. The authors found that the apparent activation energies of the H/D exchange were independent of the acidity of the zeolites. The values of the activation energies were 60, 86 and 26 kJ · mol^{-1}, which are much lower than the calculated activation energies presented by the authors of [93, 96, 97], as well as the experimentally obtained values in papers [25, 30, 95]. Similar activation barriers were reported by Vaylon et al. [100] for H-ZSM-5, H-mordenite and H-beta zeolites, I.e. 77, 74 and 43 kJ · mol^{-1}, respectively. The authors [85, 100] assumed the lower activation barriers for the zeolites to be connected with higher Lewis's acidities of the materials.

So far, there is the lack of studies related to the heterogeneous H/D exchange between methane and proton-conducting oxides and the focus of the researchers has been related to the H_2/D_2 exchange over proton-conducting oxide systems [101–104]. For the first time, the studies of the H/D exchange between methane and proton-conducting oxides in the temperature range 400–800 °C were carried out in our papers [31, 54]. Using mass spectrometry, Raman spectroscopy, ^{1}H NMR and DFT methods we analysed the mechanism of the methane activation over $La_{1-x}Sr_xScO_{3-\gamma}$ as a function of Sr content and temperature. It was found that the oxides were able to incorporate hydrogen from methane. ^{1}H NMR results showed that the incorporated hydrogen was located in the same position as the hydrogen incorporated from H_2O and H_2 [54, 105]. The mechanism of methane activation on $La_{1-x}Sr_xScO_{3-\gamma}$ was found to be stepwise methane dissociative adsorption with parallel formation of CH_3, CH_2, CH and C species. C species were assumed to be responsible for the formation of carbon deposit at 800 °C. It was determined with IE GPE and DFT methods that the adsorption centres of methane on $La_{1-x}Sr_xScO_{3-\gamma}$ can be related to surface oxygen vacancies and the positions between La and Sc surface atoms. The increase in strontium content was found to increase the degree of methane dissociation over $La_{1-x}Sr_xScO_{3-\gamma}$. In the case of $La_{1-x}Sr_xScO_{3-\gamma}$ with $x = 0.02$ and $x = 0.05$, only the formation of CH_3 and CH_2 was observed, with the contribution of the CH_3 formation in the H/D exchange that varied from 99 % at the lowest temperature to 80 % at the highest temperature of the experiments [54]. The binding energies for CH_3, CH_2, CH and C species calculated from DFT were −28.8, −57.2, −62.0 and −51.6 kJ · mol^{-1} in the case of stoichiometric $LaScO_3$ and −28.8, −57.2, −62.0 and −51.6 kJ · mol^{-1} in $LaScO_{3-\gamma}$ case, which is in agreement with the apparent activation energy of the mean rate of methane dissociative adsorption over $La_{1-x}Sr_xScO_{3-\gamma}$ with $x = 0.05$ equal to 51 kJ · mol^{-1} [31].

Summarising the papers devoted to oxides capable of uptaking hydrogen from methane, one can conclude that this ability drastically affects the methane activation mechanism. In the case of silica-alumina catalysts, the associative mechanism of methane adsorption becomes more favourable than the dissociative adsorption wieldy observed for simple oxides. In the case of proton-conducing oxides, the stepwise dissociation of methane over the surface becomes more favourable than only CH_3 formation, which makes the oxides closer to metal catalysts. However, the lack of papers devoted to different types of proton-conducting oxides does not allow us to make the conclusion whether this is the general trend for proton-conducting oxides or the feature of $La_{1-x}Sr_xScO_{3-\gamma}$.

The issue of unified data representation has to be addressed to the authors who studied the heterogeneous H/D exchange between methane and the zeolites materials, since they did not manage to choose the united way of presenting their results. Figure 6 represents the dependences of the activation energies of the heterogeneous H/D exchange on the Si/Al ratio. The figure shows that the data obtained in different papers using different methods have a high discrepancy, which is not conventionally observed in the isotope exchange field (see, e.g. papers devoted to $^{18}O/^{16}O$ exchange [106, 107] or the H_2/D_2 exchange [101–104]). The reason for this discrepancy is likely to be related to the different nature of the rate constants used by the authors for the H/D exchange analysis. Kramer et al. [25] and Stepanov et al. [36] used the time dependences of the mean deuterium fraction in the OH groups of the zeolites and in methane. The rate constant describing these dependences can be considered as the hydrogen heterogeneous exchange rate (r_H). The studies [30, 85] dealt with the time dependences of methane isotopologues fractions, which according to paper [31] as well as the PhD study of Shestov [46] depend at least on both r_H and the total rate of the H/D exchange r. These two types of the H/D exchange rates can have different activation barriers, since r_H depends on the rates of elementary steps and r represents the rate of the methane adsorption [31, 54, 46]. Thus, the accurate analysis of the H/D exchange kinetics between methane and zeolites can be possible only when authors use a similar, if not the same, system for the H/D exchange kinetic description as was done in the metals and simple oxides cases.

3.3. Metal-oxide composite catalysts

The analysis of the papers presented in Sections 3.1 and 3.2 showed that metals have generally higher catalytic activity for C–H bond cleavage. However, metal catalysts tend to sinter and lose their activity at higher temperatures. The sinterability of metals caused the development of composite catalysts. These composite catalysts are called oxide-supported metals, in which oxides are used to stabilise the microstructure of metals and prevent the sintering of metal particles. Another possible type of metal-oxide composite catalysts are cermets where metals and oxides are mixed and sintered to form a dense or porous ceramics [108]. The cermets are conventionally used as electrodes in electrochemical devices. It should be noted that the components of the composite catalysts have different chemical and physical properties, as well as different mechanisms of methane activation (see Sections 3.1 and 3.2). These differences can cause the interaction between metals and oxides in the composite resulting in the formation of a triple phase boundary (TPB), which can exhibit unique properties such as a specific adsorption or spillover effect, i.e. the directed diffusion of adsorbed species from the phases of the catalyst to the TPB [66, 109–118]. Thus, the analysis of the methane activation mechanisms over composite catalysts is of both fundamental and practical importance. In this section, we will discuss the papers devoted to the study of the methane activation mechanisms over the composite catalysts with the H/D exchange between methane and the catalyst, including not only metal-oxide catalysts, but also oxide-oxide catalysts and other related systems. The particular attention will be given to the triple phase boundary effect on the mechanism of methane activation.

The majority of studies on the H/D exchange between methane and composite catalysts were devoted to SiO_2 supported metals [46, 119–129]. Studies [34, 46] of the homogeneous H/D exchange in methane over pure SiO_2 revealed that SiO_2 is a totally inactive oxide with respect to methane activation. Thus, in the case of Me/SiO_2, only metals can activate C–H bond cleavage and the mechanism of methane activation over Me/SiO_2 catalysts can only be affected by the nature and microstructure of the metals.

The studies of the heterogeneous H/D exchange in mixtures of CH_4–D_2 over Ni/SiO_2 were performed in papers [119–121, 127, 129]. It was found that the kinetics of the heterogeneous H/D exchange over Ni/SiO_2 can be described as the combination of *stepwise* and *multiple exchange*. Cece and Gonzalez [119] found that the increase of Ni crystallites size from 19 to 140 Å leads to an increase in σ at 225 °C from 1.66 ± 0.2 to 2.30 ± 0.2, which indicates an increase in the contribution of *multiple exchange* process. Dalmon and Mirodatos [120] found that the addition of Cu to Ni/SiO_2 did not change the mechanism of methane activation, only the decrease in the rate of CH_3D and CD_4 formation was observed. Otsuka et al. [127, 130, 131] studied a methane decomposition mechanism over Ni/SiO_2 using IE GPE method and found that at temperatures ≥ 350 °C, the interaction of pure CH_4 and CD_4 with Ni/SiO_2 led to the decomposition of methane over Ni with the formation of a carbon filament-like deposit. The authors [127] also found the kinetic isotope effect of CD_4 and CH_4 decomposition: the rate of CH_4 decomposition over Ni at 400 °C was in 1.6 times higher than the rate of CD_4 decomposition. The ratio between the rates of CH_4 and CD_4 decomposition increased to 2.3 when Ni was preliminarily covered with the carbon deposit. Kroll et al. [129] studied a methane reforming mechanism using the H/D exchange in mixtures of CH_4, CD_4, $^{12}CO_2$ and $^{13}CO_2$ with SSITKA method. The authors found no kinetic isotope effect in the conversion of methane and carbon dioxide to CO and H_2. The comparison of the fractions of methane isotopologues at the inlet and the outlet of a reactor with the fractions calculated from the binomial distribution of D in methane showed that the fraction of CD_4 at the reactor outlet was higher than predicted from the binomial distribution one. This result allowed the authors to claim the existence of the kinetic isotope effect in the homogeneous H/D exchange of methane. However, the conclusion seems doubtful, since, according to Shestov's study [46], there are four types of methane dissociation, with only one type (4H type) to be purely statistical (see Section 2.2). Therefore, the observed deviation could be connected with the presence of different types of methane dissociation, and not with the isotope effects.

The studies of the mechanism of methane activation over Ru/SiO_2, $Pt\text{-}Rh/SiO_2$, $Pt\text{-}Ru/SiO_2$, Rh/SiO_2 using the H/D exchange in $CH_4–D_2$ mixtures were carried out in papers [122, 123, 125, 126]. The authors found that the mechanism of methane activation over the catalyst can be described with the combination of *stepwise* and *multiple* exchange processes, the same as in the case of the pure metal and alloy catalysts (see Section 3.1).

It should be noted that *multiple exchange* in the case of Me/SiO_2 catalysts in the considered papers was only described as the process of stepwise methane dissociation with the formation of adsorbed C species. Otsuka et al. [127] assumed that the dissociation can be responsible for the carbon deposition on Ni/SiO_2. Shestov in his PhD thesis [46] also described the mechanism of methane activation over Pt/SiO_2 as the stepwise.

Me/Al_2O_3 composite catalysts were studied in papers [124, 125, 132, 133]. Garden et al. [124] studied the heterogeneous H/D exchange in a mixture of $CH_4–D_2$ over 0.5 wt. % Pt-Ir on $\gamma\text{-}Al_2O_3$ support. The authors reported no dependence of k on the Pt/Ir ratio in the catalysts or any contribution of $\gamma\text{-}Al_2O_3$ in the exchange, which is unexpected if we take into account Larson and Hall [80] analysis of the H/D exchange over $\gamma\text{-}Al_2O_3$. Mirich et al. [128] studied the H/D exchange over 0.5 wt. % Pd/Al_2O_3 in a mixture of CH_4 and D_2 and found that the kinetics of the H/D exchange over Pd/Al_2O_3 can be described in terms of *stepwise* and *multiple exchange* reactions, which, according to the authors [128], occurred on the Pd surface, while the influence of Al_2O_3 was not discussed. Wei and Iglesia [133] analysed methane decomposition and methane reforming in mixtures of $CH_4–H_2O$, $CH_4–CO_2$ over Ru/Al_2O_3 and Ru/ZrO_2 catalysts (1.6 and 3.2 wt. % of Ru). The authors did not find the effect of the support on the methane activation mechanism, except for the influence on the metal phase dispersion. Khodakov et al. [132] studied the kinetics of the heterogeneous H/D exchange in $CH_4–D_2$ mixture over Pt/Al_2O_3 with different sizes of Pt particles in comparison with pure Al_2O_3. It was shown that in the temperature range 187–227 °C the pure Al_2O_3 is inactive to the methane activation, while Pt/Al_2O_3 demonstrated the *stepwise exchange* process similar to pure Pt (see Section 3.1). The effect of Al_2O_3 on the kinetics of the heterogeneous H/D exchange appeared at low sizes of Pt particles: when the size of Pt particles > 15–20 Å, the Pt/SiO_2 catalyst behaved like pure Pt, whereas when the size of Pt particles < 15–20 Å, the rate of the H/D exchange increased with the decrease of Pt particle size. This effect the authors connected with the charge transfer between Pt and Al_2O_3, resulted in the positive charging of Pt atoms, stabilising CH_3 species over Pt and destabilising hydrogen adsorbed atoms. Considering that H and CH_3 have the same adsorption sites (see Section 3.1), this positive charging makes the methane dissociative adsorption more favourable than that of molecular hydrogen.

In order to summarise the considered papers related to metal-simple oxide composites, let us compare the values of the heterogeneous H/D exchange rate (r_H) for metals, oxides, and Me/oxide catalysts. The Arrhenius plot dependences of r_H for a number of the catalysts discussed above are presented in Figure 7. The Figure shows that r_H values for Me/oxide catalysts are lower or comparable to those for metal catalysts and higher than r_H values reported for simple oxides, if we linearly extrapolate presented data to comparable temperature regions. Thus, the application of simple oxides, even as active as $\gamma\text{-}Al_2O_3$, seems to produce no active TPB centres that can sufficiently affect the methane activation over Me/oxide. These results explain, at least partially, why the role of the oxide phase and TPB was beyond the scope of the researchers, who studied the simple oxides supported by metals.

The role of the oxide phase in metal-oxide composites was extensively studied in the case of zeolites and proton-conducting oxides. The feature of the composites based on these materials is the ability of zeolites and proton-conducting oxides to uptake hydrogen from the gas phase, forming surface hydroxyls and proton defects, which can affect the mechanism of the methane activation, as was discussed in Section 3.2.

Khodakov et al. [133] studied the kinetics of the heterogeneous H/D exchange in $CH_4–D_2$ mixtures over Pt/mazzite catalyst. It was found that

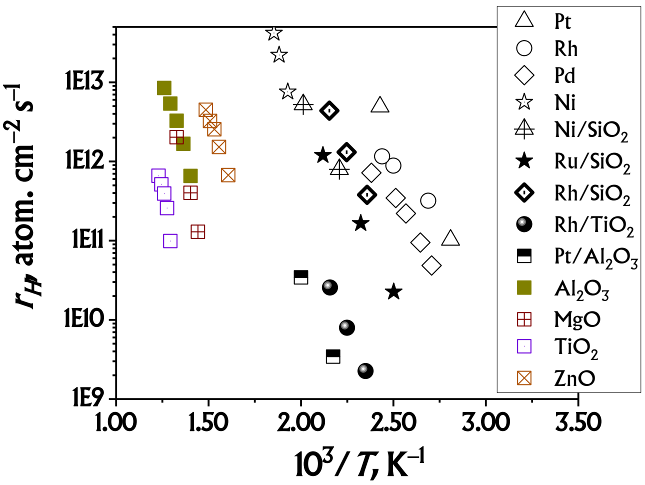

Figure 7 The Arrhenius plot of r_H for the oxide supported metals in comparison with the metals and simple oxides [58, 59, 61, 88, 120, 125, 126, 132].

the kinetics of the heterogeneous H/D exchange over Pt/mazzite corresponds to the pure Pt catalyst. The authors demonstrated that the role of mazzite zeolite in the kinetics of the H/D exchange can be associated with the inhibition of the dissociative adsorption of molecular hydrogen dissociative. The authors assumed that the inhibition was related to the formation of bridge clusters OH···Pt, which suppressed the dissociative adsorption of molecular hydrogen and promoted the dissociative adsorption of methane followed by the formation of CH_3 species over Pt.

Wen and Sachtler [134] studied the mechanism of methane activation over Pd/MFI zeolite, Cu/MFI zeolite, Fe/MFI zeolite and H-MFI zeolite catalysts in the temperature range 200–500 °C using the heterogeneous H/D exchange in the mixtures of CH_4–D_2 method. The authors found Pd/MFI zeolite to be the only active catalyst in the respective temperature range. The kinetics of the heterogeneous H/D exchange over the catalyst corresponded to the *stepwise exchange* reaction, which can also be observed in the case of the heterogeneous H/D exchange over pure Pd. The studies of the molecular hydrogen dissociative adsorption on Pd/MFI zeolites showed the existence of two types of clusters responsible for the dissociative adsorption: Pd_n and $[Pd_n–H_z]^{z+}$.

Stepanov et al. [36] studied the kinetics of the heterogeneous H/D exchange between methane and Zn/H-BEA and H-BEA zeolites in the temperature range 160–290 °C using ^{1}H NMR method with measuring the sum signal related to all methane isotopologues. To describe the kinetics of the H/D exchange, the authors used a kinetic model, which included *stepwise exchange* between methane and SiOHAl groups of the zeolite with an additional reaction of the exchange between SIOHAl and SIOH groups. The calculated values of the apparent activation energies of the heterogeneous H/D exchange between methane and the catalysts were 138 and 86–88 kJ · mol^{-1} for H-BEA and Zn/H-BEA catalysts, respectively. The decrease in the apparent activation energy of the exchange in Zn/H-BEA the authors described by two mechanisms. The first was the dissociative adsorption of methane over ZnO clusters with the formation of CH_3 species and the attachment of free H species to SiOAl groups of the zeolite. The second was the molecular adsorption of methane through the formation of an activated complex between CH_3 species, Zn^{2+} cations and H species formed after the methane dissociation. Although the authors of [36] did not speak directly about TPB, the presented mechanisms described the increased activity of the Zn/H-BEA catalyst in terms of metal-gas-zeolite centres, i.e. TPB. Thus, the increased activity of Zn/H-BEA corresponded to the specific adsorption of methane on the TPB of the catalyst.

Arzumanov et al. [135] studied the mechanism of methane activation over H-ZSM-5, In^+/H-ZSM-5 and InO^+/H-ZSM-5 (MFI type) in the temperature range 180–285 C using the same technique as Stepanov et al. [36]. It was found that the r_H values for In^+/H-ZSM-5 and InO^+/H-ZSM-5 catalysts were 1 and 2 times higher than the values for H-ZSM-5. The apparent activation energies of the heterogeneous H/D exchange were 118 ± 9, 127 ± 27 and 74 ± 6 kJ · mol^{-1} for H-ZSM-5, In^+/H-ZSM-5 and InO^+/H-ZSM-5 catalysts, respectively. The authors proposed a methane activation mechanism that contained the formation of a two-centred activated complex Zeolite–(O)In^+–(CD_4)–(H)O–Zeolite, which can further be deactivated with the release of CD_3H or with the formation of OIn^+–CD_3 by the methane dissociation. In paper [136] Arzumanov and co-workers used the same interpretation of the mechanism of methane activation over Zn^{2+}/H-ZSM-5 zeolites. Thus, the TPB in the catalysts was also considered by the Arzumanov et al. as the centre of the methane specific adsorption.

Gabrienko et al. [137–140] studied the heterogeneous H/D exchange between methane and Ga/H-BEA, Ag/H-ZSM-5, Zn^{2+}/H-ZSM-5, ZnO/H-ZSM-5 Cu^{2+}/H-ZSM-5 and CuO/H-ZSM-5 catalysts in comparison with the respective zeolites. The authors used the same methods as the authors of [36, 135, 136], since they are from the same research group. The increase in the r_H values and the decrease in the apparent activation energy of the heterogeneous H/D exchange were observed for all studied composites in comparison with the pure zeolites. The effect of r_H increase and E_a decrease was described by the authors of [137–140] in the same way as in papers [36, 135, 136]. The summarized values of the apparent

Table 3 – The apparent activation barriers of the heterogeneous H/D exchange for the Me/zeolite, zeolite and oxide catalysts.

Catalyst	Ea, kJ mol^{-1}	Ref.
H-BEA	138 ± 23	36
H-ZSM-5	118 ± 9	135
Zn/H-BEA	86 ± 5	36
Ga/H-BEA	101 ± 6	137
Ag/H-ZSM-5	94 ± 6	138
Zn^{2+}/H-BEA	96 ± 9	139
ZnO/H-BEA	93 ± 5	139
In^{+}/H-ZSM-5	127 ± 27	136
InO^{+}/H-ZSM-5	74 ± 6	136
Cu^{2+}/H-ZSM-5	102 ± 10	140
CuO/H-ZSM-5	105 ± 31	140
ZnO	134 ± 7	88
Ga_2O_3	163 ± 8	88

activation energies of the heterogeneous H/D exchange for composite zeolites studied in papers [36, 135–140] in comparison with simple oxides are presented in Table 3. The table shows that the apparent activation energies of the metal-zeolite and oxide-zeolite catalysts are lower than those for the pure oxides and zeolites. It should also be noted that in Section 3.1 we have shown the correlation between the activation barrier of the H_2 and methane adsorption over the metals. The activation barriers of the H_2 adsorption in the case of Ag and Cu are the highest among metals, which means that the activation barriers of methane adsorption are also likely to be the highest (about 300–400 kJ · mol^{-1} if we extrapolate the dependences presented in Figure 3 (b)). Thus, the lower activation barriers observed for metal/zeolite catalysts compared to these values for pure zeolites, oxides, and metals can only be explained by the composition effect of the specific adsorption sites formed by both zeolite and metal atoms, which supports mechanisms proposed by the authors of [36, 135–140].

In our recent paper [65], we studied the methane activation mechanism over Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ (50 wt. % Ni) proton-conducting cermet using H/D exchange in the mixture of CD_4–H_2 with different mol. % of CD_4. The five types of exchange theory was used to describe the obtained results (see Section 2.2). To reveal the mechanism of the methane activation, the comparative analysis of data from papers [24, 54, 141] for Ni, pure $La_{0.9}Sr_{0.1}ScO_{2.95}$, and H_2/D_2 exchange over Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ (50 wt. % Ni) was performed using the same theory. It was found that the mechanism of methane activation over Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ is similar to that over pure Ni and was connected with *stepwise* and *multiple exchange* reactions. The TPB of Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ did not show the specific activity for the methane dissociative adsorption. However, the TPB was found to be active as the centre of directed surface diffusion of H adsorbed atoms (spillover effect), which resulted in the increase of *multiple exchange* compared to pure Ni ($\sigma = 3.29$ in the Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ case and $\sigma = 2.31$ in the Ni case at 350 °C). This spillover effect was first observed in our paper [141] with the H_2/D_2 exchange over Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$. The low TPB activity with respect to the methane dissociative adsorption can be connected with the different intervals of Ni (100–400 °C) and $La_{0.9}Sr_{0.1}ScO_{2.95}$ (400–700 °C) activities.

Summarising the studies devoted to Me/zeolite and Me/proton-conducting oxide catalysts, let us consider the composition dependences of the heterogeneous H/D exchange rate for the ZnO/H-BEA and Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ catalysts calculated from data presented in papers [54, 65, 88, 120, 139]. The dependences are shown in Figure 8 in comparison with the composition dependences of r_H calculated from linear combination of the pure phases rates. The figure demonstrates that composition dependences of r_H for the ZnO/H-BEA catalyst at 0.8 wt. % mole fraction have a maximum, while the dependences for N-$La_{0.9}Sr_{0.1}ScO_{2.95}$ show higher curvature in comparison with the linear combination of r_H related to the pure phases. Thus, both the specific adsorption centres of methane at the TPB and the surface diffusion of hydrogen to the TPB can promote the methane activation. Considering these results, one can conclude that the ability of zeolites and proton-conducting oxides to uptake hydrogen from the gas phase has the drastic effect on the methane activation mechanism over Me-oxide catalysts, promoting the C–H bond dissociation in methane through the creation of the TPB, which can behave as the methane specific adsorption centre or as the centre of the hydrogen adatom diffusion. These centres make Me-zeolites and Me-proton-conducting oxide composites promising catalysts for the methane activation in comparison with the Me/simple oxides, metal, and simple oxide catalysts.

3.4. Other catalytic systems

This section is dedicated to the discussion of studies related to the kinetics of the homogeneous and the heterogeneous H/D exchange between methane and catalytic materials that are not capable with the sections described above. The catalysts presented in this section have different unique properties that could affect the methane activation mechanism.

The first type of these specific catalysts are carbide catalysts. In contrast to metals and oxides, carbides have structural carbon atoms able to interact with methane from the gas phase. Naito and co-workers [142] studied the

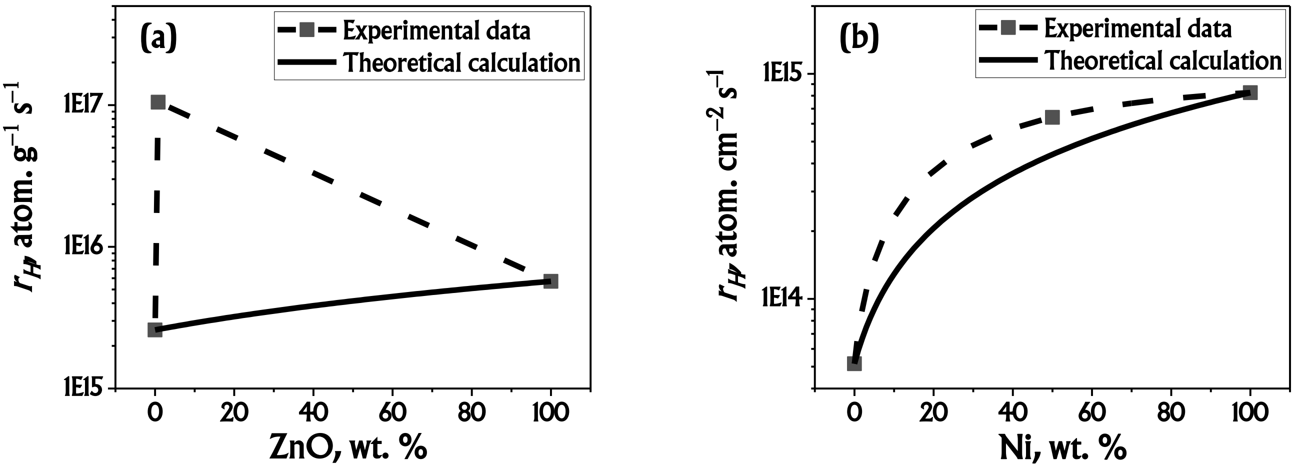

Figure 8 The composition plot of (a) mass-specified values of the heterogeneous H/D exchange rate for ZnO/ H-BEA; (b) area specified values of the heterogeneous H/D exchange rate for Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ calculated from data [54, 65, 88, 120, 139].

methane activation mechanism over 5 % Mo_2C/Al_2O_3, 5 % Mo_2C/SiO_2, 5 % Mo_2C/ZrO_2, 5 % $Mo_2C/C_{activated.}$, 5 % Mo_2C/CeO_2, 5 % Mo_2C/TiO_2 using the H/D exchange in mixtures of CH_4–CD_4, CD_4–H_2 and $^{12}C/^{13}C$ exchange in mixtures of $^{13}CH_4$–$^{13}CO_2$. It was found that the interaction of the $^{13}CH_4$–$^{13}CO_2$ mixture with $Mo_2{}^{12}C$ resulted in the formation of ~ 1 : 1 mixture of ^{12}CO and ^{13}CO. The authors assumed that the formation of ^{12}CO during the process was caused by structural ^{12}C oxidation of Mo_2C by CO_2 with the formation of carbon vacancies in Mo_2C occupied by methane carbon. However, the obtained results cannot be interpreted unambiguously on account of the simultaneous course of the exchange and conventional chemical reactions between the gas phase and the catalyst. By comparing the rates of CH_3D formation in the mixtures of CH_4–CD_4 and CD_4–H_2 the authors revealed the inhibiting effect of H_2 on the H/D exchange between methane and the catalysts under study. A similar inhibiting effect was observed in papers [24] for the Ni catalyst, while in the case of Ni/SiO_2, Ni-$La_{0.9}Sr_{0.1}ScO_{2.95}$ [65, 127] and oxide catalysts (see Section 3.2) the addition of H_2 catalysed the methane activation. The authors suggested that the mechanism of methane activation over 5 % Mo_2C/Al_2O_3 included the participation of three types of methane adsorption sites, i.e. Mo_2C, Al_2O_3 and TPB. It should be noted that the inhibition effect can indicate that the main centres of the H_2 and methane adsorption are the same (see Section 3.1), whereas the oxides have the different centres of the H_2 and methane adsorption (see Section 3.2). Therefore, the suggestion that Al_2O_3 in Mo_2C/Al_2O_3 plays the role of methane adsorption centres is doubtful. Brush et al. [143] studied the H/D exchange between methane and Mo_2C, as well as the $^{12}C/^{13}C$ exchange between $^{13}CH_4$ and $Mo_2{}^{12}C$ in the temperature range 25–800 °C using the PIE technique. The experiments revealed no $^{12}CH_4$ formation, indicating the absence of interaction between methane and carbon atoms of the carbide, which contradicts the results of Naito et al. [142]. The authors only found CH_3D formation at 800 °C, which was described in terms of methane dissociative adsorption.

Oxide supported non-metals and zeolites are another type of methane activation catalysts. Quanzhi and Amenomiya [36] tried to improve the catalytic properties of Al_2O_3 using H_2SO_4 and K_2CO_3 as acid and base activators. The homogeneous H/D exchange experiments in methane over 4.5 wt. % H_2SO_4/Al_2O_3 and 9.1 wt. % K_2CO_3/Al_2O_3 revealed that the former catalyst became completely inactive in methane atmospheres, while the latter became in 5 times less active than pure Al_2O_3. Hua et al. [144, 145] studied the heterogeneous H/D exchange between methane and unpromoted as well as Al_2O_3 promoted SO_4^{2-}/ZrO_2, which can be considered as promising catalysts for alkanes isomerisation. The authors found that the apparent activation barriers of SO_4^{2-}/ZrO_2, SO_4^{2-}/ZrO_2-Al_2O_3 and $SO_4^{2-}/ZrO_2/Al_2O_3$ were 93, 94 and 96 kJ · mol^{-1}, which are lower than the values for H-ZSM-5 zeolite (see Table 3). The reported r_H values were the same within the error limit and varied from $1 \cdot 10^{-9}$ to $9 \cdot 10^{-9}$ mol · g^{-1} · s^{-1}. The author proposed a similar mechanism of the methane activation as in the papers devoted to zeolites (see Section 3.2) and considered the formation of a two-centre CH_5 activation complex, depicted in Figure 9 (a). Jentoft and Gates [146] studied the heterogeneous H/D exchange between methane and $AlCl_3$/sulfonic acid resin, SO_4^{2-}/ZrO_2, Fe-Mn/SO_4^{2-}/ZrO_2. It was found that the value of the apparent activation energy for Fe-Mn/ SO_4^{2-}/ZrO_2 was 116 ± 14 kJ mol^{-1}, which is comparable with the values for pure zeolites (see Table 3). The rate of the exchange for

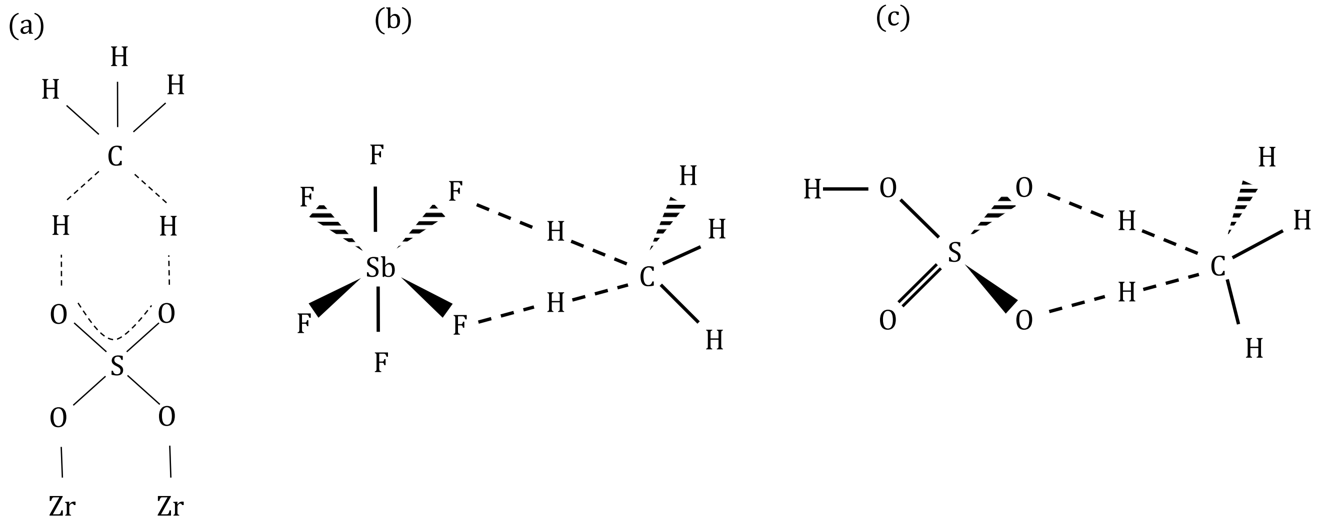

Figure 9 The associative activated complexes of methane over (a) sulfated zirconia, (b) HSO_3F SbF_5 and (c) H_2SO_4 [144, 145, 151].

the catalyst was the same as in the H-ZSM-5 zeolite case in the temperature range 300–400 °C, whereas $AlCl_3$/sulfonic acid resin was active only below 150 °C, since at that temperature it decomposed. Nevertheless, at this temperature, the catalyst was 3 orders of magnitude more active than Fe-Mn/ SO_4^{2-}/ZrO_2 and H-ZSM-5.

Hanada et al. [147] reported the study of the H/D exchange between methane and Al_2O_3 supported base KND_2, which was considered by the authors to be the catalyst of methane isomerization. Using the infrared spectroscopy method, the authors found that the catalyst was able to activate the C–H bond cleavage in methane at room temperature. The mechanism of KND_2 activation was considered to be the reversible splitting of a N–D/N–H bond, although the mechanism of methane activation was not described by the authors.

Another exotic type of methane activation catalysts are liquid superacid catalysts [35, 148, 149, 150, 151]. These catalysts have structural hydrogen, which, as was shown in Sections 3.2 and 3.3, can drastically affect the mechanism of methane activation. In contrast to conventional solid methane activation catalysts, the surface of liquids is not completely stable, which results in constant movement of liquid molecules from the bulk to the surface and to the gas phase and vice versa. All these features make liquid superacids interesting catalytic systems for methane activation. Let us discuss papers related to the study of the H/D exchange between methane and liquid superacids.

In paper [35], Walspurger et al. studied the kinetics of the heterogeneous H/D exchange between CH_4 and $DSO_3F \cdot SbF_5$ superacid at 30 °C using ^1H NMR with the discrimination of lines related to different methane isotopologues. The authors found that the kinetics of the heterogeneous H/D exchange between methane and the catalyst can be described by the *stepwise exchange*-like kinetic model. The increase of SbF_5 mole fraction in the superacid from 19 to 45 mol. % led to the decrease of the apparent activation energy of the exchange from 97 to 84 $kJ \cdot mol^{-1}$. The values of the apparent enthalpy of the H/D exchange were independent of the SbF_5 mole fraction, whereas the values of the apparent entropy of the exchange increased with the SbF_5 mole fraction from −25 to −15 $J \cdot mol^{-1} \cdot K^{-1}$. The authors did not report the mechanism of the methane activation over the acid, although in papers [148–151] the authors supposed the formation of CH_5^+ cation from protons of the acid and methane (see Figure 9 (b)).

Goeppert et al. [151] studied the heterogeneous H/D exchange between methane and 98 wt. % D_2SO_4 + 2 wt. % D_2O in the temperature range 250–340 °C. The apparent activation energy of the heterogeneous H/D exchange was 175 $kJ \cdot mol^{-1}$. Using DFT, the authors proposed the mechanism of the methane activation as the formation of a two-centre CH_5 activated complex, which is presented in Figure 9 (c).

Summarising the studies presented in this section, one can conclude that the authors who investigated the methane activation over the oxide supported non-metals and liquid catalysts considered the methane activation as associative adsorption with the formation of a CH_5 activated complex. Similar mechanisms were suggested to describe the methane activation over the silica-alumina catalysts. One of the possible reasons for this similarity is the similar acid-base nature of the active adsorption centres over the liquid acids, silica-alumina and oxide supported non-metals. In the case of carbide catalysts, the authors preferred to describe the mechanism of the methane activation as the dissociative adsorption, which is likely to be connected with the consideration of carbon vacancies as the methane adsorption centres.

4. Conclusions

In this paper, a comprehensive analysis of literature data related to the H/D exchange studies of the methane activation mechanism over catalysts has been carried out.

Infrared spectroscopy, mass spectroscopy and ^{1}H NMR were compared in terms of their applicability in the obtaining of the most accurate kinetic information related to the hydrogen isotope redistribution between methane and a catalyst. Mass spectrometry was shown to be the most flexible method for the analysis of hydrogen isotope redistribution in the gas phase, while ^{1}H NMR was found to be the most relevant method for the simultaneous studies of the isotope composition in both the gas and solid phases.

The four most general kinetic approaches for the H/D exchange description were considered with respect to the accuracy and mathematical rigorousness of the H/D exchange kinetic description. The first-order chemical kinetics and Kemball-Anderson approaches were found to be the simplest and roughest approaches, whereas Shestov-Muzykantov and the five types of exchange theory approaches can be considered as the most mathematically rigorous approaches with, however, the most complicated systems of differential equations.

The critical analysis of the methane activation studies over metals, oxides, metal-oxide composites, oxide supported non-metals and liquid catalysts was carried out in terms of the homogeneous and heterogeneous H/D exchange rates, the activation energies of the H/D exchange and the intermediate species involved in the exchange reactions.

The direct relationships between the H_2 and CH_4 adsorption over metals were found. H_2 was found to inhibit the H/D exchange over the metals. In the case of the oxide catalysts, the addition of H_2 has the promoting effect on the H/D exchange. The difference in the H_2 effect on the kinetics of the H/D exchange over the metals and oxides was suggested to be connected with the difference in the adsorption centres of H_2 and CH_4 over the oxides. The increase of the Me–O bond length in simple binary oxides was shown to increase the activation barriers of the homogeneous H/D exchange in the absence of H_2.

The composite effect was found in the zeolite-supported metals, zeolite-supported oxides and metal-proton-conducting oxide cermet cases, with the absence of the effect in the simple binary oxide-supported metals case. The composition effect was described with the triple phase boundary, which can exhibit the methane specific adsorption properties or behave as the centre of hydrogen surface diffusion (spillover effect).

The two types of methane activation mechanisms on the catalysts were described, i.e. the dissociative and associative adsorption of methane. The stepwise dissociative adsorption of methane was considered to be responsible for the methane activation over the metals, simple binary oxides and proton-conducting oxides catalysts, whereas the associative adsorption of methane was considered to be responsible for the methane activation over the zeolites and liquid catalysts.

Supplementary Materials

No supplementary materials are available.

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None.

Author contributions

Dmitriy Zakharov: Conceptualization; Writing – original draft; Writing – Review & Editing; Visualisation.

Conflict of interest

The authors declare no conflict of interest.

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