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Nonoxidative Conversion of Methane and *n*-Pentane over a Platinum/Alumina Catalyst

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Abstract—Methane adsorption on the Pt–H/Al_2O_3 and Pt/Al_2O_3 catalysts begins at $T = 475$°C and is accompanied by the appearance of hydrogen in the reaction medium. At a higher temperature is raised to 550°C, the amount of adsorbed hydrogen increases to 1.1 and 0.8 mol/(mol Pt), respectively. According to the calculated degree of methane dehydrogenation on platinum sites at $T = 550$°C, the H/C ratio is 1.3 (at/at) for the Pt–H/Al_2O_3 catalyst and 1.5 (at/at) for the Pt/Al_2O_3 catalyst. The introduction of *n*-pentane into the reaction medium increases the yield of aromatic hydrocarbons (benzene and toluene) by a factor of 8.8 over the arene yield observed in individual *n*-pentane conversion. A mass spectrometric analysis of the arenes obtained with the Pt/Al_2O_3 catalyst has demonstrated that 37.5% of the adsorbed methane is involved in the methane–*n*-pentane coaromatization yielding benzene and toluene.

Keywords: methane, *n*-pentane, isotope-ratio mass spectrometry, aromatic hydrocarbons
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INTRODUCTION

Methane is the main component of natural gas and is viewed as the most promising raw material for petrochemistry. Because of the high stability of the methane molecule, it was long believed that nonoxidative methane conversion is possible only above 1000°C. At present, the possibility of methane chemisorption on a catalyst at moderate temperatures (200–450°C) with the formation of CH_x fragments and hydrogen molecules is discussed in the literature [1–4]. Most of the relevant studies were aimed at investigating the two-step nonoxidative homologation of methane into C_{2+} hydrocarbons. Many transition metals supported on various materials have been tested in this reaction to date [1, 4–6].

There has been a work dealing with one-step methane conversion over Pd–Co/SiO_2 and Pt–Co/NaY catalysts [7]. In addition, in the last five years there have been studies on the catalytic activity of particular faces of metal crystals, such as Ni(100), Ni(111), and Ni(553) [8], and on the possibility of methane chemisorption on platinum and palladium clusters supported on graphenes and carbon nanotubes [9].

Thus, while two-step nonoxidative methane homologation has been investigated fairly well for a large number of supported metal oxide catalytic systems typically containing 3–12 wt % metal, data concerning the co-conversion of methane with higher hydrocarbons are practically lacking. The only works in this area deal with the co-conversion of methane with propane [10–12] and hexane [13] over zeolite catalysts.

Here, we report methane chemisorption on a platinum/alumina catalyst containing 1 wt % Pt and the capacity of CH_x fragments to undergo co-conversion with *n*-pentane.

EXPERIMENTAL

Catalyst Preparation

For preparing the catalyst, the initial γ-Al_2O_3 support ($S_{BET} = 177.7$ m^2/g, $V_{pore} = 0.68$ cm^3/g, $d_{av} = 154$ Å) was loaded with oxalic acid (3 wt %) from its aqueous solution. The resulting sample was dried at 120°C and calcined in flowing dry air at 500°C. Next, platinum (1 wt %) was deposited onto the sample from an H_2PtCl_6 solution mixed with dilute hydrochloric acid (1 wt %) and dilute acetic acid (1.5 wt %). The resulting catalyst was dried at 120°C, calcined in flowing dry air at 500°C, and reduced in a hydrogen atmosphere at 500°C. The dispersion of platinum in the catalyst, determined by oxygen titration of hydrogen preadsorbed on the catalyst surface [14, 15], was 96%.

Catalytic Tests

The adsorption properties of the catalysts were studied in the temperature range from 20 to 550°C at $CH_4 : Pt = 10 : 1$ (mol/mol) in a perfect-mixing reactor. A catalyst sample was pre-reduced in flowing dry hydrogen at 500°C for 1 h. For investigating methane adsorption on the surface of the catalyst containing pre-adsorbed hydrogen ($Pt{-}H/Al_2O_3$), the reactor was cooled to room temperature. Thereafter, the reactor was fed with a methane : argon = 50 : 50 (vol/vol) mixture. Argon was used as the internal standard. For investigating methane adsorption on the "clean" surface of the reduced sample (Pt/Al_2O_3), argon was supplied into the reactor for 2 h at $T = 500$°C to remove weakly bound hydrogen from the catalyst surface; thereafter, the catalyst was cooled to room temperature in flowing argon and was analyzed for hydrogen content. Next, the methane : argon = 50 : 50 (vol/vol) mixture was fed into the reactor. After the study of the adsorption properties of the catalyst, *n*-pentane was added to methane in the reaction mixture ($C_5H_{12} : CH_4 = 4 : 1$, mol/mol) at $T = 550$°C. The $C_5H_{12} + CH_4$ mixture was in contact with the Pt/Al_2O_3 catalyst for 3 min. *n*-Pentane was chosen to be the model hydrocarbon for the following two reasons. Firstly, *n*-pentane does not undergo direct aromatization and the arenes appearing in the reaction medium can be obtained only by methane–*n*-pentane coaromatization or result from secondary reactions of *n*-pentane with products of its cracking. Secondly, *n*-pentane is thermodynamically more stable than its higher homologues. Therefore, if it is demonstrated that methane and *n*-pentane can undergo co-conversion over the Pt/Al_2O_3 catalyst, it will be possible to state that the higher homologues of *n*-pentane will participate in the reaction as well and their reaction will be thermodynamically still more favorable.

The methane that was used in the experiments was 99.9 vol % pure and was ^{13}C-enriched to the extent of 99.9 at %. *n*-Pentane was 99.9 wt % pure.

Isotope-Ratio Mass Spectrometry

The stable carbon isotopes (^{13}C and ^{12}C) in the feedstock and reaction products were quantified on a DELTA V Advantage magnetic-sector mass spectrometer (Thermo Fisher Scientific, Germany). The sample was separated in a capillary column (60 m × 0.25 mm × 1.0 mm, Thermo Fisher Scientific) in the temperature-programmed mode while raising the temperature from 40 to 180°C at a rate of 3°C/min at a constant carrier gas (helium) flow rate of 0.8 mL/min. The components leaving the chromatograph were directed to an oxidation reactor ($T = 1030$°C), and the, resulting CO_2 was passed through a Nafion drier (Thermo Fisher Scientific, Germany) and a ConFlo IV gas preparation block (Thermo Fisher Scientific) and was then admitted in the ion source of the mass spectrometer. The sample to be analyzed was ionized by an electron impact. The isotopic composition of the sample was determined versus a standard CO_2 gas. The ^{13}C content was calculated using the VPDB international standard.

^{13}C NMR Spectroscopy

The ^{13}C NMR spectra of the catalysts after experiments were recorded on an Avance_400 NMR spectrometer (Bruker, Germany) with an SB4 multinuclear probe using a single-pulse technique with high-power broadband proton decoupling (hpdec pulse program, Bruker). A catalyst samples, ground in an agate mortar, was placed in a zirconia rotor (Bruker, Germany; $d = 4$ mm) with a plastic (Kel–F) cap, and a spectrum was recorded at a spinning frequency of 1 kHz at a magic angle of 54.7° to the constant magnetic field direction. The Larmor frequency was 100.4 MHz. The pulse repetition time was 20–30 s. The external standard was tetramethylsilane. The experiment duration was 48 h.

Carbon Deposit Content Determination

Carbon deposits on the catalyst surface were quantified by automatic coulometric titration on an AN-7529 express analyzer (Russia).

RESULTS AND DISCUSSION

To see whether methane–*n*-pentane co-conversion is thermodynamically allowable, we calculated the change in the Gibbs energy of the system (ΔG). Figure 1a how the change in the Gibbs energy varies with temperature for the formation of benzene, toluene, xylenes, and *n*-hexane for the methane–*n*-pentane mixture. It follows from these calculations that benzene formation is possible near 800 K (527°C); toluene formation, at 830 K. The formation of xylenes can occur only at $T > 950$ K. Note that *n*-hexane formation is impossible in the temperature range examined.

The extent of a reaction can be characterized in terms of equilibrium conversion (X_{eq}). The numerical values of X_{eq} for the thermodynamically possible reactions in the system are presented in Fig. 1b [16]. Clearly, at $T = 823$ K (550°C) X_{eq} for benzene formation is about 17%. The same equilibrium conversion for toluene formation is reached at $T = 900$ K; for the formation of xylenes, it is reached at $T > 1000$ K because of the lower thermodynamic probability of the reaction taking place.

Methane adsorption on the platinum/alumina catalyst containing pre-adsorbed hydrogen ($Pt{-}H/Al_2O_3$) begins at 475°C (0.1 mol/(mol Pt)), as is shown in Fig. 2a. As the reaction temperature is elevated to 550°C, the amount of adsorbed methane increases to

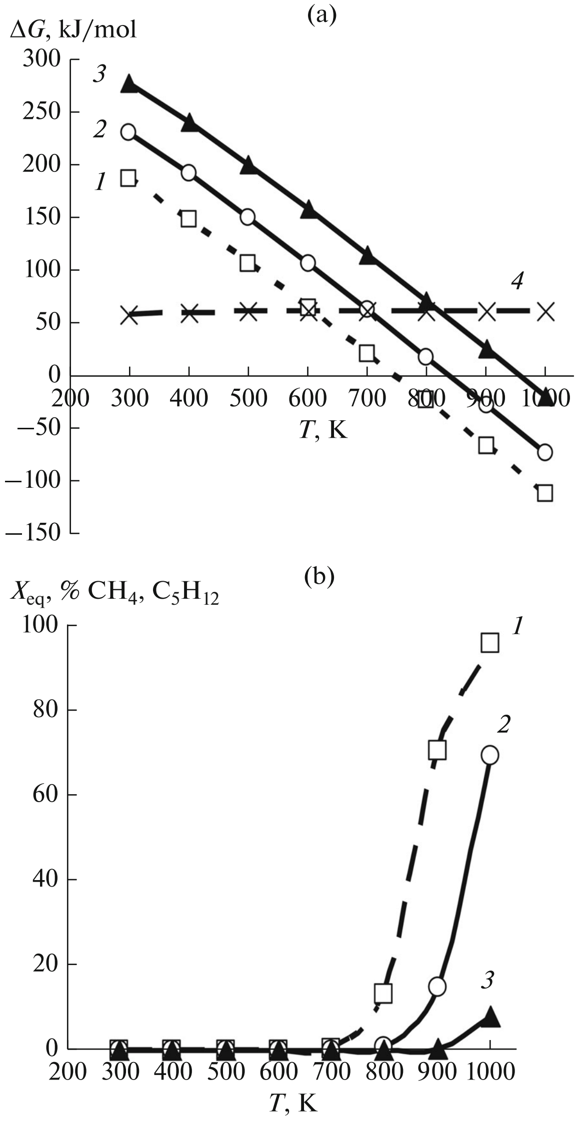

Fig. 1. (a) Change in the Gibbs energy and (b) equilibrium conversion of methane and *n*-pentane as a function of the reaction temperature for the reactions (*1*) $CH_4 + C_5H_{12} = C_6H_6 + 5H_2$, (*2*) $2CH_4 + C_5H_{12} = C_7H_8 + 6H_2$, (*3*) $3CH_4 + C_5H_{12} = C_8H_{10} + 7H_2$, and (*4*) $CH_4 + C_5H_{12} = C_6H_{14} + H_2$.

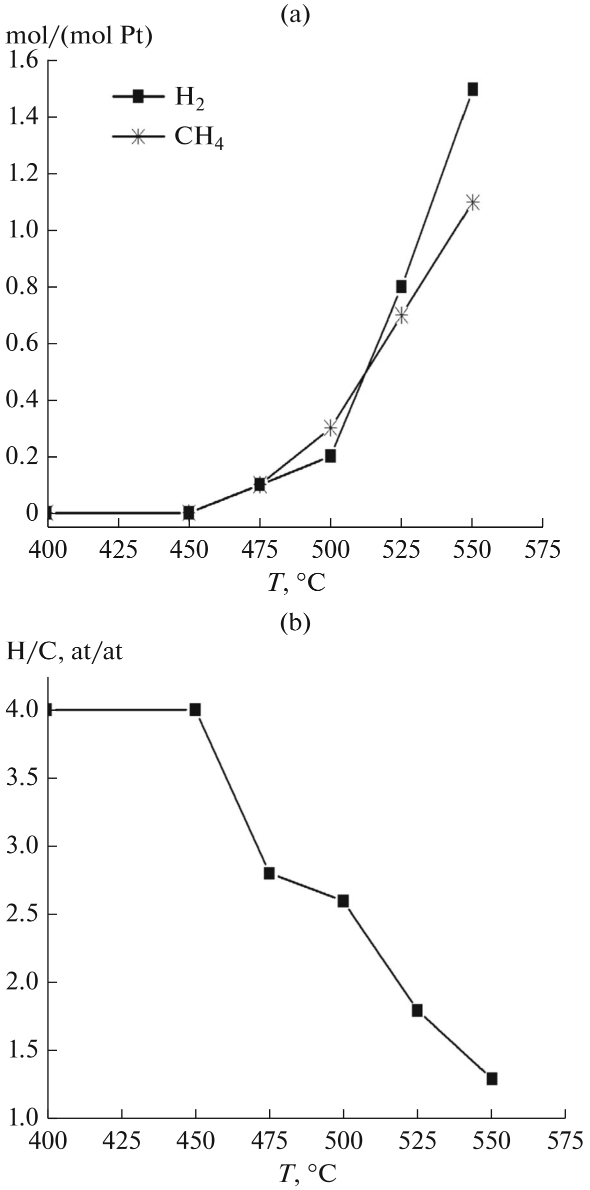

Fig. 2. (a) Amount of methane adsorbed and the amount of hydrogen released as a result of methane adsorption for the Pt–H/Al_2O_3 catalyst; (b) H/C ratio in the adsorbed hydrocarbon fragments.

1.1 mol/(mol Pt). The onset of methane adsorption at $T = 475°C$ is accompanied by the appearance of hydrogen in the reaction medium. Raising the temperature to 550°C increases the H_2 content to 1.5 mol/(mol Pt). It follows from these data that hydrogen adsorption is dissociative and slightly overstoiciometric. Apparently, owing to hydrogen diffusion from platinum to the support (spillover), part of the adsorbed methane, undergoing dehydrogenation, is transferred to the Al_2O_3 surface. Along with the hydrogen that is released as a result of methane adsorption, the hydrogen desorbed from the surface of the Pt–H/Al_2O_3 catalyst is present in the reaction medium; the amount of the latter was thoroughly measured in our earlier study [17]. The 1.5 (mol H_2)/(mol Pt) value was obtained by subtracting the amount of weakly bound hydrogen desorbed from the catalyst from the total amount of H_2 in the system.

From the amounts of adsorbed methane and released hydrogen, we derived the degree of methane dehydrogenation over the platinum sites (Fig. 2b). At the onset point of adsorption, the average H/C value for the hydrocarbon fragments on the surface is 2.8 at/at. An increase in the adsorption temperature leads to a deeper methane hydrogenation down to H/C = 1.3 (at/at). It turns out that a considerable part of methane is low-active at 550°C. Apparently, the CH_x fragments resulting from methane adsorption are structurally inhomogeneous.

Methane adsorption on the catalyst surface containing no pre-adsorbed hydrogen (Pt/Al_2O_3) also begins at $T = 475$°C (Fig. 3a). The amount of methane converted in this case is 0.3 mol/(mol Pt), and the amount of released hydrogen is 0.1 mol/(mol Pt). Raising the reaction temperature to 550°C increases the amount of methane adsorbed to 0.8 mol/(mol Pt) and increases the amount of hydrogen released to 1.0 mol/(mol Pt). Calculation of the degree of hydrogenation of adsorbed methane on platinum sites demonstrates (Fig. 3b) that, at the onset temperature of adsorption ($T = 475$°C), H/C = 3.3 (at/at). Elevating the temperature to 550°C causes further hydrogen abstraction yielding H-deficient hydrocarbon fragments with H/C = 1.5 (at/at) on the surface.

The above data on methane adsorption on the $Pt{-}H/Al_2O_3$ and Pt/Al_2O_3 catalysts suggest that, in both cases, methane conversion begins at $T = 475$°C. However, at 550°C the amount of methane adsorbed for the $Pt{-}H/Al_2O_3$ sample (1.1 mol/(mol Pt)) is larger than for Pt/Al_2O_3 (0.8 mol/(mol Pt)). Furthermore, calculations demonstrated that methane on the Pt/Al_2O_3 catalyst is dehydrogenated to a lesser extent (H/C = 1.5 (at/at)) than methane on the $Pt{-}H/Al_2O_3$ catalyst (H/C = 1.3 (at/at)).

A comparison between the above data and the results obtained for the two-step methane homologation yielding C_{2+} hydrocarbons [1–4] reveals significant distinctions between the methane adsorption regularities in these processes. When the two-step methane conversion process was studied on low-dispersion catalysts with a high metal content (which was usually the case), adsorption began near 150°C and, once a temperature of $T = 350$°C was reached, only unreactive graphite-like fragments were identified on the surface. In the Pt/Al_2O_3 catalyst, platinum sites are highly dispersed because of the relatively low metal content and there are no Pt–Pt bonds [18]. This is likely the reason why the onset of adsorption shifts to higher temperatures ($T = 475$°C). This fact is thermodynamically favorable for methane–*n*-pentane co-conversion taking place.

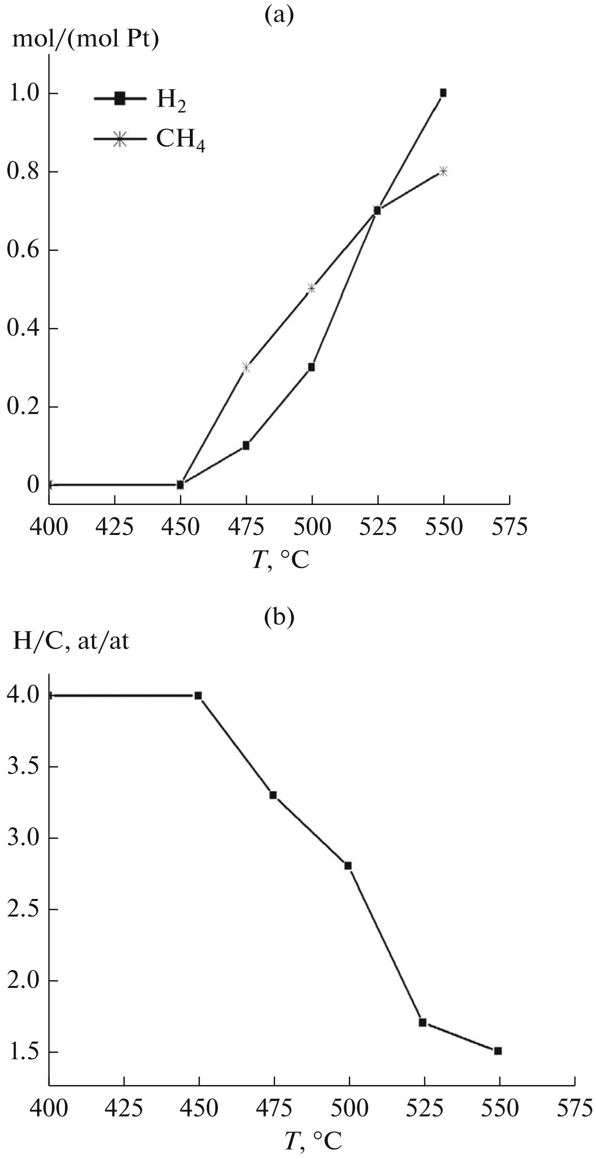

Fig. 3. (a) Amount of methane adsorbed and the amount of hydrogen released as a result of methane adsorption for the Pt/Al_2O_3 catalyst; (b) H/C ratio in the adsorbed hydrocarbon fragments.

We studied the conversion undergone by *n*-pentane over the $Pt{-}H/Al_2O_3$ catalyst at $T = 550$°C (Table 1). The $n\text{-}C_5H_{12}$ conversion value was 84.5%. The hydrogen yield was 5.6 mol/(mol Pt), and the yield of gaseous hydrocarbons (methane, ethane, propane, butanes) was 25.9 mol/(mol Pt). The reaction products contained a small amount of i*so*pentane (0.3 mol/(mol Pt)). Aromatic hydrocarbons were represented by benzene (0.9 mol/(mol Pt)) and toluene (0.4 mol/(mol Pt)). For investigating the reactivity of the CH_x fragments appearing on the $Pt{-}H/Al_2O_3$ surface as a result of methane decomposition, *n*-pentane was introduced into the reactor at 550°C (Table 1). This increased the *n*-pentane conversion to 87.3%. The hydrogen yield was 6.0 mol/(mol Pt), and the yield of gaseous hydrocarbons, which were dominated by methane, was 30.3 mol/(mol Pt). The total arene yield increased by a factor of 2.5 (benzene, 1.1 mol/(mol Pt); toluene, 2.1 mol/(mol Pt)) over the arene yield observed for individual *n*-pentane.

Thus, although for the $Pt{-}H/Al_2O_3$ catalyst the H/C ratio at $T = 550$°C is 1.3 (at/at), the hydrocarbon fragments that have formed from methane react with *n*-pentane to yield benzenea. Therefore, on the surface of this catalyst there are catalytically active fragments

Table 1. Hydrocarbon yields on the converted *n*-pentane basis for the Pt–H/Al_2o_3 catalyst

Reaction products, mol/(mol Pt)	Initial reactants	
	n-pentane*	methane + *n*-pentane**
Hydrogen	5.6	6.0
Methane	7.7	22.8
Ethane	8.6	5.1
Propane	7.5	1.8
Butanes	2.1	0.6
Isopentane	0.3	0.4
n-Pentane	6.2	5.1
Benzene	0.9	1.1
Toluene	0.4	2.1

* Pentane conversion: 84.5%.

** Pentane conversion: 87.3%.

Reaction conditions: T = 550°C, CH_4/Pt = 10/1 (mol/mol), CH_4/C_5H_{12} = 1/4 (mol/mol).

Table 2. Hydrocarbon yields on the converted *n*-pentane basis for the Pt/Al_2O_3 catalyst

Reaction products, mol/(mol Pt)	Initial reactants	
	n-pentane*	methane + *n*-pentane**
Hydrogen	5.9	6.5
Methane	17.1	17.7
Ethane	15.5	3.2
Propane	10.4	0.7
Butanes	4.7	0.0
Isopeentane	2.1	0.4
n-Pentane	8.4	8.3
Benzene	0.4	3.1
Toluene	0.1	1.3

* Pentane conversion: 79.0%.

** Pentane conversion: 79.3%.

Reaction conditions: T = 550°C, CH_4/Pt = 10/1 (mol/mol), CH_4/C_5H_{12} = 1/4 (mol/mol).

along with H-deficient ones. This is also indicated by the fact that the benzene yield in the methane–*n*-pentane co-conversion is higher than in the conversion of *n*-pentane alone.

In the case of the individual conversion of *n*-pentane over the Pt/Al_2O_3 catalyst, the *n*-pentane conversion value reaches 79.0% (Table 2). The amount of hydrogen released in this case is 5.9 mol/(mol Pt), and the yield of C_1–C_4 gases is 47.7 mol/(mol Pt). The benzene yield (0.4 mol/(mol Pt)) and toluene yield (0.1 mol/(mol Pt)) are lower than the corresponding yields observed for Pt–H/Al_2O_3.

In the case of *n*-pentane admitted to adsorbed methane, the *n*-C_5H_{12} conversion is 79.3% (Table 2). The amount of hydrogen in the reaction medium is 6.5 mol/(mol Pt), and the amount gaseous hydrocarbons there is 21.6 mol/(mol Pt). The arene yield increases markedly: the benzene yield rises to 3.1 mol/(mol Pt); the toluene yield, to 1.3 mol/(mol Pt).

The catalytic testing data for the Pt–H/Al_2O_3 and Pt/Al_2O_3 samples indicate that, on passing from the methane–*n*-pentane co-conversion to the conversion of individual *n*-pentane, the product composition does not change qualitatively and only quantitative changes take place, primarily in the proportions of the resulting gaseous hydrocarbons. The main advantage of the hydrocarbon co-conversion process is that it affords a higher arene yield. For example, the arene yield in this process is 2.5 higher with the Pt–H/Al_2O_3 catalyst and 8.8 higher with the Pt/Al_2O_3 catalyst.

The aromatic hydrocarbons resulting from enriched methane–*n*-pentane co-conversion over Pt/Al_2O_3 were analyzed by isotope-ratio mass spectrometry. The study of the isotopic composition of carbon demonstrated that the benzene molecules contain 0.2 mol ^{13}C, and the toluene molecules contain 0.1 mol ^{13}C (Fig. 4). Therefore, of the total amount of synthesized benzene (3.1 mol/(mol Pt)), 0.2 mol/(mol Pt) benzene molecules are obtained with the participation of $^{13}CH_4$; of the total amount of synthesized toluene (1.3 mol/(mol Pt)), 0.1 mol/(mol Pt) toluene molecules contain ^{13}C from $^{13}CH_4$. From these data and the amount of methane adsorbed at 550°C on the Pt/Al_2O_3 catalyst (0.8 mol/(mol Pt)), it can be derived that 37.5% of the adsorbed $^{13}CH_x$ molecules are involved in the formation of aromatic hydrocarbons. It is apparently this proportion of the catalytically active $^{13}CH_x$ fragments resulting from methane adsorption occur on platinum sites at H/C = 1.5 (at/at). The rest benzene molecules (2.9 mol/(mol Pt)) and toluene molecules (1.2 mol/(mol Pt)) form without involving $^{13}CH_4$; most likely, they form from gaseous hydrocarbons resulting from *n*-pentane cracking. It is clear from the above calculations that the increase in the arene yield on passing from the conversion of *n*-pentane alone to the co-conversion of $^{13}CH_4 + C_5H_{12}$ is inconsistent with the amount of arenes formed from the reacted methaney. It is likely that the methane present in the reaction medium along with *n*-pentane shifts the reaction toward aromatization rather than cracking.

After the $^{13}CH_4$ + *n*-C_5H_{12} co-conversion experiment, 0.2 wt % carbon (3.4 mol/(mol Pt)) was deposited on the Pt/Al_2O_3 surface. Calculations demonstrated that the methane remaining adsorbed on platinum sites (62.5%) can yield 0.5 mol carbon per mole of Pt. The rest of the carbon deposit, 2.9 mol/(mol Pt), likely resulted from *n*-pentane decomposition.

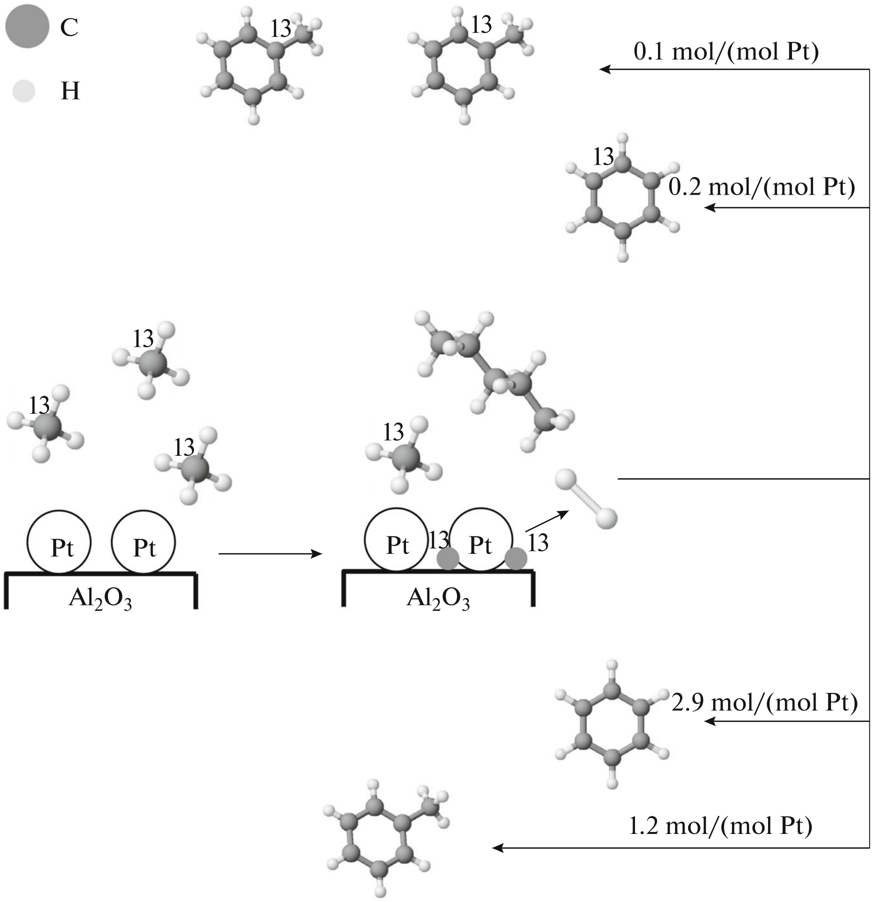

Fig. 4. Isotopic composition of carbon in aromatic hydrocarbons.

The structure of the carbon deposit was studied by ^{13}C NMR spectroscopy. Figure 5 shows a fairly intensive maximum in the resonance range of sp^2-hybridized carbon, whose chemical shift is 120–130 ppm. This maximum indicates the presence of a coke deposit in the form of nanosized graphene clusters on the catalyst surface. The observed graphene structures might result both from the decomposition of adsorbed methane and from the condensation of arene precursors that had formed via the reaction between methane and *n*-pentane. For the sake of comparison, we present, in Fig. 5, the ^{13}C NMR spectrum of the Pt/Al_2O_3 sample that has been tested in $^{12}CH_4$–*n*-pentane coconversion. Clearly, the signal at 120–130 ppm in this spectrum is much weaker than the same signal in the spectrum of the previous catalyst sample, even though the experimental conditions were identical. Therefore, ^{13}C is definitely present in the structure of the graphene clusters in the experiments involving $^{13}CH_4$.

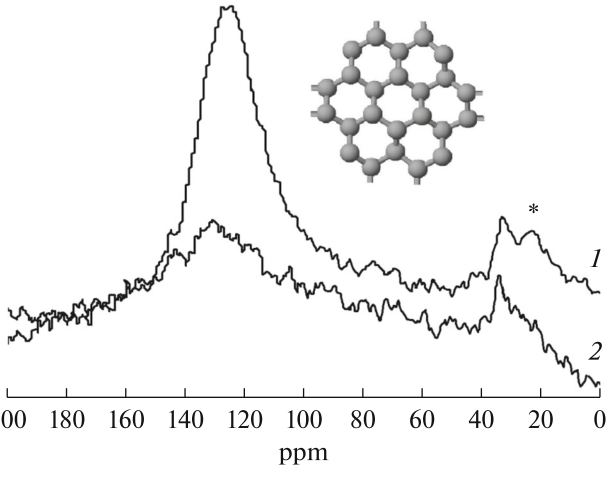

Fig. 5. ^{13}C NMR spectra of the Pt/Al_2O_3 catalyst recorded after the (*1*) $^{13}CH_4 + C_5H_{12}$ and (*2*) $^{12}CH_4 + C_5H_{12}$ coconversions.

The less intense and less broad signal at 30 ppm is evidence of the presence of *n*-alkanes on the catalyst surface. Most likely, these are traces of unreacted *n*-pentane. The magic angle spinning satellites in the spectrum are labeled with symbol *.

Thus, this study demonstrated that methane adsorption on the $Pt–H/Al_2O_3$ and Pt/Al_2O_3 catalysts begins at 475°C, accompanied by the appearance of hydrogen in the reaction medium. as the temperature is raised to 550°C the amount of methane adsorbed increases to 1.1 and 0.8 mol/(mol Pt), respectively. According to the calculated degree of methane dehydrogenation on platinum sites at 550°C, the H/C ratio for the Pt—H/Al_2O_3 catalyst is 1.3 (at/at) and the same ratio for the Pt/Al_2O_3 sample is 1.5 (at/at). The introduction of *n*-pentane into the methane-containing reaction medium markedly increases the yield of aromatic hydrocarbons (benzene and toluene). An isotope-ratio mass spectrometric analysis of the arenes resulting from the reaction over the Pt/Al_2O_3 catalyst demonstrated that 37.5% of the adsorbed methane is involved together with *n*-pentane in benzene and toluene formation. Apparently, it is this proportion of the catalytically active $^{13}CH_x$ occurs on platinum sites at H/C = 1.5 (at/at). Unreacted methane and the condensed arene precursors that have resulted from the interaction between methane and *n*-pentane but have not been desorbed into the gas medium remain as graphene clusters on the catalyst surface.

It was demonstrated that aromatic hydrocarbons can be synthesized on highly dispersed platinum via the co-aromatization of methane and *n*-pentane over a platinum/alumina catalyst under mild reaction conditions.

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