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Transformation of methane over platinum supported catalysts at moderate temperature

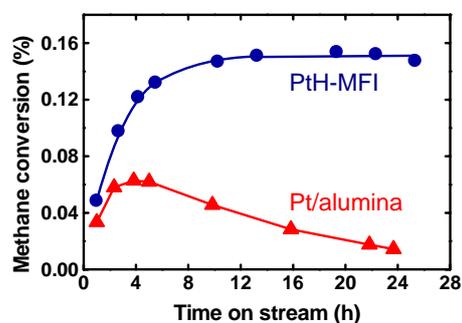
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Research Highlights

- > Methane is converted in ethane during many hours over Pt catalysts at 370 °C.
- > Reaction proceeds via transformation of surface CH_x and C species.
- > Stable catalyst performance is associated with slow coupling of carbon species.
- > Other transition metals (Co, Fe, Ru, Rh) could be active in methane conversion.

Graphical Abstract



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Abstract

Non-oxidative methane reactions over solid catalysts are normally regarded as high temperature reactions (700 °C and above). Here we show that methane can be converted into ethane during many hours over two platinum supported catalysts at 370 °C.

Analysis of the experimental data and DFT calculations, available in the literature, suggests that this reaction proceeds via formation and subsequent coupling of surface carbonaceous species (CH_x and C) and that the relatively stable catalyst performance is associated with slow coupling of carbon species. Our work indicates that other transition metal (Co, Fe, Ru, Rh) supported catalysts should be active in methane conversion into ethane at similar and, possibly, lower temperatures. Thus, further research into these catalytic systems would furnish new experimental data on formation and transformation of surface CH_x species, which are believed to be involved in such reactions as Fischer-Tropsch synthesis, methanation and methane steam reforming.

Keywords: Methane; Activation; Reaction; DFT; Platinum; Transition metals

1. Introduction

Methane, the principal component of natural gas and an important greenhouse gas, is nowadays considered as a vast potential feedstock for production of chemicals [1-6]. Different approaches to methane activation and transformation have been investigated extensively during the last 3 decades, but the direct efficient methane transformation has yet to be developed [1-6]. For long time non-oxidative methane reactions have been regarded as high temperature reactions (700 °C and above) due to high thermodynamic stability of methane and associated unfavorable thermodynamics of its transformation at lower temperatures [3,5,7]. However, it would be a mistake to underestimate the importance of the research into these reactions at lower temperatures, since it could improve our understanding of the mechanisms of C–C bond formation at low/moderate temperatures, which is currently an area of significant scientific interest.

Activation of methane at relatively low temperatures (150-250 °C) was first demonstrated by Kemball [8-10] in the early 1950s in the experiments on CH₄–D₂ exchange on metal films. Since that time methane activation on various metal catalysts at low and moderate temperatures was confirmed by many research groups using different catalytic and surface science techniques (papers [7,11-13] and references therein) and, more recently, was explained by the DFT studies, which were comprehensively reviewed by van Santen et al. [14]. Curiously, very little data on conversion of pure methane into gaseous products was reported and discussed in these experimental and theoretical studies. Of particular relevance to our communication is the work on methane activation and transformation into hydrocarbons over transition metal supported catalysts via two-step reaction sequence [7,15-20], when methane is activated under relatively mild conditions with formation of C₁ surface intermediates

(step 1), which produce C_{2+} hydrocarbons upon hydrogenation (step 2). In these experiments, Amariglio et al. [16-18] and Solymosi et al. [19] observed formation of ethane during the first step of the cycle. The ethane formation rate decreased during 5-20 minutes of the reaction and no data on ethane formation was reported at longer time. Obviously, ethane formation was taking place under transient conditions and it is therefore of interest to investigate the possibilities of a steady state (or quasi steady state) methane conversion into ethane (or higher hydrocarbons) over transition metal supported catalysts. Such an investigation appears to be important, since it may contribute to our understanding of the mechanisms of C–C bond formation from C_1 surface species at low/moderate temperatures.

Our recent study of conversion of methane/benzene mixture into toluene has suggested [21] that reasonably stable transformation of pure methane into ethane could be achieved over Pt-containing H-MFI zeolite catalyst at such low temperature as 370 °C. The aim of this work was to test this suggestion and to attempt to get new insights into mechanisms of activation and transformation of pure methane over transition metal supported catalysts. To achieve this goal, we decided (i) to analyze the recently reported results of the density functional theory (DFT) studies, relevant to methane activation, and (ii) to consider the results of this analysis together with the experiments on methane transformation over Pt-containing catalysts at 370 °C.

2. Experimental

2.1. Catalyst preparation and characterization

Two Pt-supported catalysts (1 wt% Pt), defined as PtH-MFI and Pt/Al₂O₃, were prepared by incipient wetness impregnation of the H-MFI zeolite (ZEOLYST, Si/Al =

15) and γ -Al₂O₃ (Alfa Aesar, 320 m²/g), respectively, with an aqueous solution of tetraammineplatinum(II) nitrate, Pt(NH₃)₄(NO₃)₂. Prior to the reaction studies, the catalysts were dried at room temperature, calcined in air at 530 °C and then reduced in hydrogen at 500 °C. The Pt dispersion in the reduced PtH-MFI and Pt/Al₂O₃ catalysts was 12 and 33%, respectively. For kinetic studies, the catalyst powder samples were pressed into disks, crushed, and sieved to obtain catalyst particle sizes in the range of 0.25-0.5 mm. The full description of the catalyst preparation and characterization is presented in our previous publications [21,22].

2.2. Kinetic studies and thermogravimetric analysis

The catalysts were tested at atmospheric pressure in a continuous flow reactor at 370 °C. Experiments were performed with pure methane as a feed at weight hour space velocity (WHSV) of 1.26 h⁻¹, and the reaction mixture was analyzed by on-line gas chromatography, as described elsewhere [22].

After completion of the reaction (24 hours for Pt/Al₂O₃ catalyst and 25 hours for PtH-MFI catalyst), the reactor was purged by oxygen-free nitrogen (30 ml/min) for 0.5 h at 370 °C and then cooled down to room temperature in a nitrogen atmosphere. The catalyst samples were then unloaded from the reactor for further thermogravimetric analysis (TGA). Similar procedure was used earlier in the study of coke formation during benzene alkylation with ethane into ethylbenzene [23]. TGA of the discharged PtH-MFI and Pt/Al₂O₃ catalysts was performed in a Setaram TG-92 thermogravimetric analyzer following the procedure developed by Manos and coworkers [24,25]. This procedure allows one to distinguish between coke precursors, which can be removed through volatilization in N₂, and hard coke, which stays on the catalyst up to 600 °C and is removed by burning in air. In our experiments, a catalyst sample of ~50 mg was first

purged at room temperature by nitrogen (30 ml/min) for 2 h, then heated to 250 °C at the rate of 10 °C/min and kept at this temperature for 1 h in the same N₂ flow to remove adsorbed water. Then the temperature was raised (10 °C/min) to 600 °C and kept at this temperature under N₂ flow for 30 min in an attempt to remove coke precursors. Finally, nitrogen was replaced by air at the same flow rate (30 ml/min) at 600 °C, and the sample was kept under these conditions for 1.5 h.

3. Results and Discussion

3.1. Analysis of DFT calculations available in the literature

As a consequence of the significant progress in DFT calculations [14,26], theoretical descriptions of the realistic energetic profiles of various reactions have become a reality and, therefore, can be used to generate better understanding of these reactions. Methane decomposition into carbonaceous species as well as hydrogenation of these species into methane over transition metals have been studied by different research groups [14, 26-35]. However, these reactions were usually analyzed as important reaction steps in methanation [14,26,27], Fischer-Tropsch [14,28-31] and methane steam reforming [32] processes, and were not examined as a part of transformation of pure methane into larger hydrocarbons. Here we consider the available theoretical data with the focus on methane transformation.

DFT calculations of methane decomposition were reported for different transition metals [14,27,32-35], and are illustrated in Fig. 1 by the energy diagrams for this reaction on relatively flat terraces [33] and stepped [34] platinum surfaces. Fig. 1 shows that the adsorption energies for different species as well as the activation energies of transformation of these species depend on the type of the platinum surface. In general,

the adsorption of carbon (C) and CH_x ($x = 1-3$) species is stronger on stepped Pt surface, while the activation energies are higher, as a rule, for flat Pt surface. Fig. 1 reveals that the activation energy of methane transformation into $\text{CH}_3 + \text{H}$ (that is, in fact, the methane activation step) is ~ 65 and 35 kJ/mol for the flat and stepped Pt surfaces, respectively. Interestingly, regardless of the type of Pt surface, the most stable surface species are CH species and formation of carbon species requires the highest activation energy. In general, this is true for other transition metals, such as Co, Ni, Rh, Ru, Pd and Ir [14]. Moreover, for Pt surfaces, carbon species have the lowest adsorption energy (Fig. 1) and, as a consequence, should be present in the lowest concentration on the catalyst surface. Thus, the reactions between two carbon species (leading to coke formation) should be less favorable, in terms of the concentrations of the reacting species, than coupling of CH_x species with formation of C_2 hydrocarbon precursors.

The above conclusion is further enhanced by the DFT calculations reported by Hu and coworkers [29-31] for the coupling reactions between carbon and CH_x species. Indeed, for the coupling reactions involving C, CH, CH_2 and CH_3 species, the coupling $\text{C} + \text{C}$ reaction was found to have the highest activation energy (174-283 kJ/mol, depending on the metal). This result was obtained for stepped surfaces of five transition metals (Rh, Co, Ru, Fe and Re) and it is therefore likely that it will stand also for platinum. The lowest activation energies of CH_x coupling reactions over five different metals were found [31] to be 26 kJ/mol for Co and Fe, 83 kJ/mol for Rh, 89 kJ/mol for Ru and 137 kJ/mol for Re. These estimates can be compared with 102 kJ/mol for CH_x coupling over flat (111) and stepped (211) Pt surfaces [35], and with 102 and 65 kJ/mol for $(\text{CH}_2 + \text{CH})$ and $(\text{CH}_3 + \text{CH})$ reactions, respectively, over Ru (0001) surface [28].

The DFT results discussed above reveal that activation of methane and its further transformation into C₂ hydrocarbons (ethane and/or ethene) via coupling reactions is quite possible at moderate temperatures for a range of transition metals due to relatively low activation energies of the reaction steps involved. Moreover, the reaction is expected to be quite stable, since the steps of coke formation appear to occur at slow rates. The prediction regarding methane activation agrees well with the experiments on CH₄-D₂ exchange on metal films at 150-250 °C [8-10] and the experiments [16-20] on methane decomposition into carbonaceous species and hydrogen over transition metal supported catalysts (Ru, Rh, Pd, Pt, Co, Ir) at such low temperatures as 100-200 °C. However, the prediction of the stable methane conversion into C₂ hydrocarbons has no experimental support. As noted in the Introduction section, the formation of ethane was indeed observed at low temperature (250 °C), but the catalysts were losing their activity during 5-20 minutes of the reaction [16,19]. Hence, the steady state catalyst performance was not achieved. This is an important result, since it questions the validity of the DFT calculations that predict slow catalyst deactivation due to slow coke formation. Another possibility of the disagreement between the experimental and theoretical results might be associated with very low equilibrium conversion of methane into ethane at 250 °C (below 0.1%). Such low steady state conversion (if it was in truth achieved) could be simply considered as zero conversion and, therefore, 'missed'.

3.2. Experimental study of methane transformation on PtH-MFI and Pt/Al₂O₃ catalysts

To clarify the reason of the disagreement between the existing experimental and theoretical results and to examine the possibility of relatively stable methane conversion, we decided to test two Pt-supported catalysts in the reaction of pure

methane at 370 °C. The choice of the temperature and the first catalyst, PtH-MFI, was based on our recent work [21] that demonstrated highly selective and stable conversion of methane and benzene into toluene at 370 °C over this catalyst. The second catalyst, Pt/Al₂O₃, was chosen as a more conventional catalyst. Both catalysts contained 1 wt% of platinum, but the Pt dispersion was different: 12 and 33% on the PtH-MFI and Pt/Al₂O₃ catalysts, respectively. The equilibrium conversion of pure methane in ethane and hydrogen was estimated, using the thermodynamic data [36], to be 0.25% at 370 °C.

Transformation of pure methane over the PtH-MFI and Pt/Al₂O₃ catalysts was studied in a continuous flow reactor during 24-25 hours. Fig. 2A shows that methane conversion was increasing during the first 4-6 hours of the reaction reaching 0.15 and 0.06% over PtH-MFI and Pt/Al₂O₃ catalysts, respectively. With further increase in time, slow Pt/Al₂O₃ catalyst deactivation was observed, while the performance of the PtH-MFI catalyst was stable. Ethane was the sole carbon containing product over the Pt/Al₂O₃ catalyst and the major product over the PtH-MFI catalyst (Figs.2B and 2C). In the latter case, benzene and toluene were also produced but their amounts were much smaller than the amount of ethane. Interestingly, benzene and toluene were not observed even in trace amounts on the Pt/Al₂O₃ catalyst, which did not contain Brønsted acid sites (BAS). Thus, it is possible that formation of benzene and toluene over PtH-MFI catalyst was following the dehydrocyclodimerization (aromatization) mechanisms over bifunctional catalysts, which were first proposed by Csicsery [37] and were later supported by kinetic modeling studies by Lukyanov et al. [38,39].

The initial (transient) period of the reaction (Fig. 2) is likely to be linked to the accumulation of the surface carbonaceous species (e.g. CH₃, CH₂, CH, C, C₂H_x) on the Pt particles of the catalysts. Formation of such species from methane on the surface of

transition metals is predicted by the DFT calculations (see Fig. 1 and discussion above), and was considered by different authors [7,12,13,16-20,40] for methane decomposition on a number of transition metals. One can expect that the accumulation of these species on Pt active sites would lead to changes in the catalyst performance that was indeed observed in the experiments (Fig. 2). Formation of surface carbonaceous species should lead to formation of H₂ in the gas phase, as schematically illustrated below by the reactions generating the surface CH₃ and C species.



Hydrogen released in the reactions (1) and (2) cannot be accounted for by formation of the hydrocarbons detected in the gas phase. Hence, one would expect to observe hydrogen formation in excess of formation of the gaseous hydrocarbon products. The experimental data in Fig. 3 support this expectation. Indeed, Fig. 3A demonstrates that the experimentally determined hydrogen concentration is significantly higher during the transient period than the hydrogen concentration, which corresponds to formation of the hydrocarbons observed in the gas phase. The latter was calculated on the basis of the experimentally determined concentrations of these hydrocarbons (ethane, benzene and toluene) and the stoichiometric equations for the reactions shown below.



The difference between the experimental and calculated hydrogen concentrations is shown in Fig. 3B and corresponds to hydrogen released during formation of the surface carbonaceous species. This difference is decreasing rapidly during the first 4-6

hours of the catalyst operation and then stabilizes at $\sim 0.05\%$ and $\sim 0.15\%$ for the PtH-MFI and Pt/Al₂O₃ catalysts, respectively. Such a pattern is consistent with two possible processes, which may take place at the catalyst surface and release H₂ in the gas phase. The first process (accumulation of surface carbonaceous species) appears to be completed in about 4-6 hours (Fig. 3) and is likely responsible for the transient catalyst operation during this time (Fig. 2). The second process is taking place during all 25 hours of the experiment and produces H₂ in much smaller amounts than the first one (Fig. 3). Comparison of the data in Figs. 2 and 3 suggests that this, second process is associated with formation of inactive surface carbon species that are responsible for the slow deactivation of the Pt/Al₂O₃ catalyst after 4-6 hours on stream. The deactivation of the PtH-MFI catalyst is not observed in our experiments and this agrees with the low concentration of hydrogen formed on this catalyst (Fig. 3B).

Let us now consider the extent of methane transformation into ethane over two catalysts tested in this work. As noted above, the equilibrium conversion of methane into ethane and hydrogen was estimated to be 0.25% assuming stoichiometric methane conversion (Eq. (3)). This is not the case in our experiments, since additional hydrogen was produced during formation of the surface carbonaceous species and, with the PtH-MFI catalyst, during formation of benzene and toluene as well. With this additional hydrogen taken into account, we determined that for 4 hours on stream the experimental methane conversion into ethane was about 74 and 60% of the equilibrium methane conversion for the PtH-MFI and Pt/Al₂O₃ catalysts, respectively. Hence, the methane conversion over the PtH-MFI catalyst was quite close to the equilibrium conversion, and one may suggest that this could be the reason for the observed stable performance of this catalyst. Indeed, in general, the effect of coke on the conversion would be more

pronounced at lower conversions than at conversions approaching equilibrium values.

To test this suggestion, we analyzed the coke content on two catalysts used in this study.

The thermogravimetric profiles for the PtH-MFI and Pt/Al₂O₃ catalysts are shown in Fig. 4. The obtained data reveal that only 0.3 wt% of carbonaceous species are retained by the PtH-MFI catalyst and that these species are desorbed from the catalyst in the flow of nitrogen, when the catalyst is heated from 250 to 600 °C (Fig. 4A).

Interestingly, no species, which could be considered as hard coke [24,25], are present on this catalyst (hard coke can be removed by burning only). In our opinion, these results provide a solid explanation for the observed stable performance of the PtH-MFI catalyst (Fig. 2) and demonstrate that the retained carbonaceous species are unlikely to be of a graphitic nature (i.e. built by the reactions of carbon (C) species). The latter result is in excellent agreement with the analysis of the DFT studies (see section 3.1) that indicates slow rates of C + C coupling reactions.

The data in Fig. 4B show that the Pt/Al₂O₃ catalyst contains both the coke precursors (0.8 wt%) and hard coke (0.4 wt%). Thus, this catalyst would be expected to deactivate much faster than the PtH-MFI one, and this is exactly what is observed in the catalytic experiments (Fig. 2). It is also worth to note that the difference in the amounts of the carbonaceous species retained by two catalysts used in this work agrees well with the difference in the amounts of hydrogen, which was assumed to be produced over these catalysts during formation of the surface carbonaceous species (see Fig. 3B). The data in Fig. 4B reveal that the amount of the hard coke (possibly, of graphitic nature) is 2 times lower than the amount of the coke precursors, thus pointing out to the slower rates of C + C coupling reactions in comparison with the rates of the coupling reactions between CH_x species.

4. Conclusions

The experimental data and DFT calculations considered in this communication suggest that methane conversion into ethane and hydrogen proceeds via formation and subsequent coupling of surface carbonaceous species (CH_x and C) and that the relatively stable catalyst performance is associated with slow coupling of carbon species with formation of coke on the catalyst surface. Although the absolute values of methane conversions are low (due to thermodynamic limitations), our finding is important in principle, since it demonstrates that non-oxidative continuous methane transformation is possible at moderate temperatures (previously, two step catalytic cycle was considered as a necessity [7,15-20]). The discussion of the reasons of the different activities as well as stabilities of the two catalysts used in this work constitutes a separate subject for future study. Here we would like to comment that this difference is likely to be related to the different electronic properties of the Pt particles on these catalysts due to the different nature of the supports [41-43]. The size of the Pt particles, which is probably different on two catalysts because of the different Pt dispersion, is also likely to contribute to the difference in their catalytic performance [14,26,42,43]. Finally, as mentioned above, the presence (or absence) of BAS in the catalysts could also affect their performance.

Analysis of the recent DFT calculations [14,26-35] points out that other transition metal catalysts, such as Co, Fe, Ru and Rh, might be active in stable methane transformation in ethane at moderate temperatures (because of the relatively similar activation energies of the reaction steps involved in this reaction). Hence, further research into these catalytic systems (including Pt-supported catalysts) could furnish new data on formation and transformation of surface CH_x species, which are believed to

be involved in the mechanisms of such reactions as Fischer-Tropsch synthesis, methanation and methane steam reforming [14,26,28-33]. These, new data can be used for independent evaluation of the theoretical studies of these industrially important reactions and are likely to contribute to better understanding of their mechanisms. Of particular interest would be experiments with methane at low temperatures (~ 250 °C), including experiments in the presence of CO, H₂ and H₂O.

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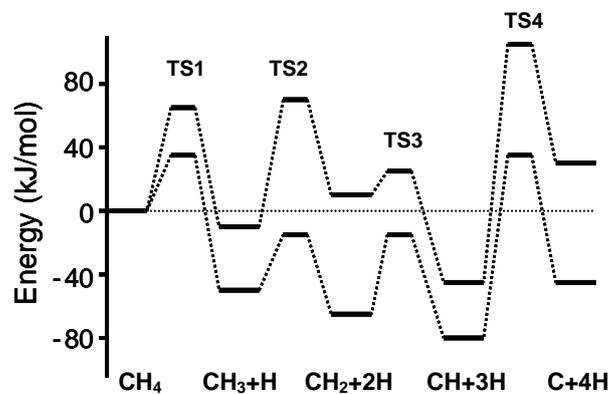


Fig. 1. Reaction energy diagrams for transformation of methane into carbon and hydrogen chemisorbed on flat Pt(111) terraces and stepped Pt(110)(1×2) surfaces. All energies are referenced to methane in the gas phase and the clean surfaces. The top diagram for the flat Pt surface is based on the data in ref. 33, and the bottom diagram for the stepped Pt surface is based on the data in ref. 34. TS stand for transition state.

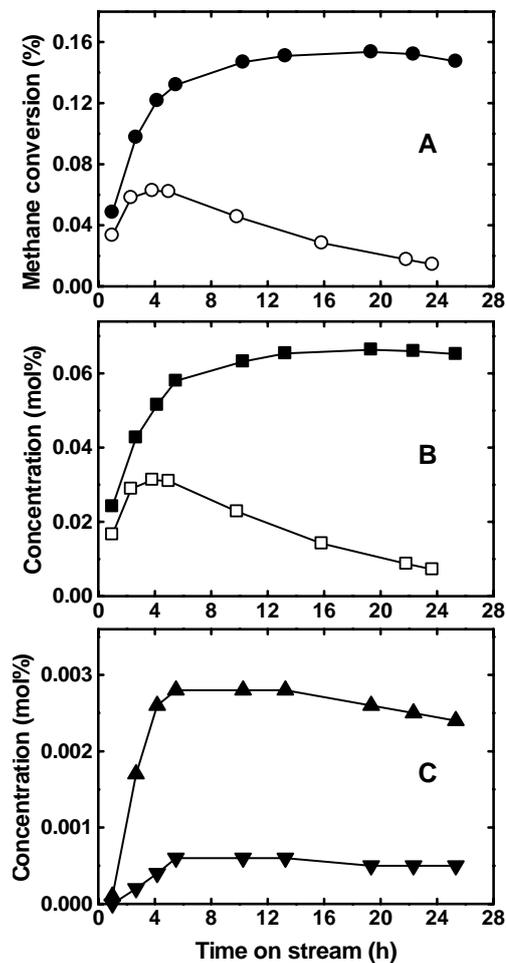


Fig. 2. Effect of time on stream on methane conversion and product formation over PtH-MFI (solid symbols) and Pt/Al₂O₃ (open symbols) catalysts: (A) Methane conversion (●,○), (B) concentration of ethane (■,□), and (C) concentrations of benzene (▲) and toluene (▼). Reaction was carried out at 370 °C with pure methane as a feed and at weight hour space velocity of 1.26 h⁻¹.

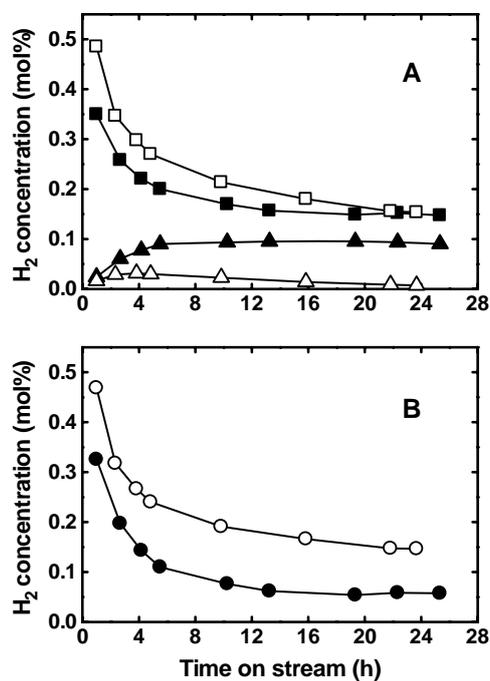


Fig. 3. Effect of time on stream on hydrogen formation over PtH-MFI (solid symbols) and Pt/Al₂O₃ (open symbols) catalysts. (A) Experimental (■,□) and calculated (▲,△) values, and (B) the difference between the experimental and calculated values (●,○). Calculated values for hydrogen correspond to formation of all hydrocarbon products observed in the gas phase (see text for explanation). Reaction conditions are given in the legend of Fig. 2.

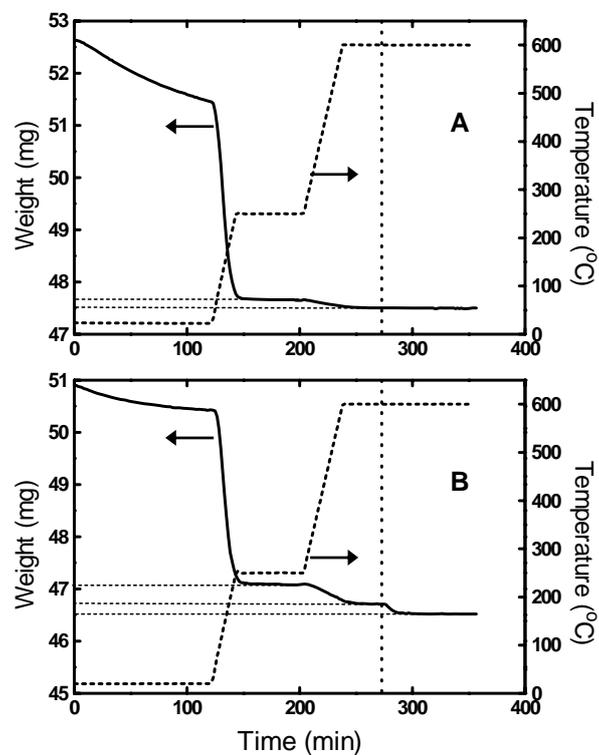


Fig. 4. Thermogravimetric profiles for (A) PtH-MFI and (B) Pt/Al₂O₃ catalysts after 25 and 24 hours of the reaction, respectively. Reaction conditions are given in the legend of Fig. 2. TGA procedure is described in section 2.2, and the vertical dotted line corresponds to the switch from the nitrogen to the air flow.