Selective and stable benzene alkylation with methane into toluene over PtH-MFI bifunctional catalyst

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ABSTRACT

This paper demonstrates for the first time that methane reacts with benzene over bifunctional PtH-MFI catalyst with selective and stable formation of toluene at such low temperature as 370 °C. Our results show that the catalyst activity increases during the initial period of the reaction (∼4 h) and that this increase is likely associated with the modification of the Pt particles with the surface carbonaceous species (e.g. CH_3, CH_2, CH, C, and C_2H_x). The highest catalyst activity is observed at time on stream (TOS) of 4 h, when toluene selectivity is around 96 mol% and conversions of benzene (4.5%) and methane (0.53%) are close to the equilibrium conversions (5.6% and 0.62% for benzene and methane, respectively). At higher TOS, the catalyst activity declines slowly and at TOS of 23 h conversions of benzene and methane are around 3.8% and 0.45%, respectively. To the best of our knowledge, the reaction of benzene alkylation with methane into toluene, reported in this paper, is the first example of the catalytic reaction involving methane that proceeds continuously during many hours under non-oxidizing conditions.

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1. Introduction

Methane, which is the major component of natural gas, represents very promising feedstock for production of other chemicals. However, high thermodynamic stability and very low reactivity of methane make its activation and selective transformation into more valuable (and reactive) chemicals extremely difficult. Therefore, in spite of a significant research effort during the last two decades, the problem of methane activation and selective transformation has not been resolved and represents one of the most exciting and important challenges (both from the theoretical and practical viewpoints) in the field of catalysis [1–5].

One of the possible ways to tackle this problem is to decrease the thermodynamic limitations of methane transformation by involving methane in reactions with other hydrocarbons. Examples of this approach include studies by two research groups, which concluded that methane was reacting with alkenes (ethene, propene, and n-butene) [6,7] and alkanes (propane and n-hexane) [6] at 400–600 °C over H-MFI zeolites modified by different metals (e.g. gallium, silver, etc.). It is worth noting that the results of these studies were obtained at time on stream (TOS) of 5 min [6] and 1 h [7], because of the rapid catalyst deactivation, and have not been confirmed later on by other researchers. Moreover, these results

disagree completely with the work of the other two groups, who demonstrated that methane was not involved in the reactions with propane [8] and ethene and propene [9] over Ga-containing H-MFI catalysts under reaction conditions that were similar to the conditions reported in Refs. [6,7].

Alkylation of aromatics with methane was reported by He et al. [10–12] over modified aluminophosphate molecular sieves and zeolites. In this work the reactions were carried out in a batch reactor at 400 °C under elevated methane pressure (6.9 MPa). The incorporation of the methyl groups derived from methane into the substituted benzene and naphthalene products was confirmed, using $^{13}CH_4$, for the reactions over Cu/SAPO-5, Cu/beta and H-beta catalysts [11,12]. However, subsequent studies have established [13–15] that the presence of oxygen as a stoichiometric reactant is actually required for the formation of methylated products during transformation of methane and benzene over a number of zeolite catalysts at 400 °C in a high-pressure batch reactor. It has been proposed that oxidative methylation reaction proceeds via a two-step mechanism that involves formation of methanol as an intermediate product. The H-beta zeolite was shown to be the only one catalyst that produced methylated products in the absence of oxygen [13,15]. However, in this case it was concluded, in agreement with the earlier report by Kennedy et al. [16], that the methylated products were derived solely from the benzene reactant.

Our recent work [17,18] has demonstrated that the PtH-MFI bifunctional catalysts can be used successfully for the highly selective benzene alkylation with ethane into ethylbenzene (EB) at 370 °C. These results together with the data on methane activation

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over catalysts containing Pt and other Group VIII transition metals [19–28] have led us to the idea that the PtH-MFI catalysts could activate methane and catalyze its further reaction with benzene into toluene, as shown below:

$$CH_4 + C_6H_6 \leftrightharpoons C_6H_5CH_3 + H_2 \tag{1}$$

The present study was undertaken to test this hypothesis. We decided to perform the experiments at 370 °C with a feed comprised of 90 mol% methane and 10 mol% benzene (following the reaction conditions of our work with ethane/benzene mixtures). The PtH-MFI catalyst with a Si/Al ratio of 15 was chosen for this work, since it has shown the highest activity in benzene alkylation with ethane among three PtH-MFI catalysts of different acidity [17,18]. It is worth noting that Pt-containing MFI zeolite catalysts have not been tested in earlier studies [10–16] of transformation of methane and benzene mixtures. Thermodynamic calculations, based on the data reported by Yaws [29], have indicated that the equilibrium conversions of methane and benzene in reaction (1) should be around 0.62% and 5.6%, respectively (for the chosen reaction conditions).

2. Experimental

2.1. Catalyst preparation and characterization

H-MFI zeolite with a Si/Al ratio of 15 (ZEOLYST) was used in this study as a parent material. High crystallinity of the zeolite and the absence of other phases were confirmed by X-ray diffraction analysis. Scanning electron microscopy has shown that the size of the zeolite crystallites was in the range between 0.4 and 0.7 μm. The nature and number of acid sites in the zeolite were determined by FTIR spectroscopic experiments using pyridine as a probe molecule. FTIR spectra of the self-supported catalyst discs were collected at a resolution of $2\,cm^{-1}$ using a Bruker Equinox 55 FTIR spectrometer and a purpose-built IR cell that allowed high-temperature treatment of samples in situ [30]. Pyridine adsorption was carried out at 150 °C, after the samples were activated under vacuum (10^{-5} mbar) at 400 °C overnight. On the basis of these experiments, the number of all acid sites in the H-MFI zeolite was estimated as 535 μmol g^{-1}, and the numbers of the Brønsted and Lewis acid sites were estimated as 448 and 87 μmol g^{-1}, respectively.

The Pt-containing zeolite catalyst (1 wt.% Pt), defined as PtH-MFI, was prepared by incipient wetness impregnation of the H-MFI zeolite with an aqueous solution of tetraammineplatinum(II) nitrate, $Pt(NH_3)_4(NO_3)_2$. After impregnation the catalyst was dried slowly at room temperature (~48 h), and then calcined (in a thin layer) in a muffle furnace at 530 °C for 4 h (heating rate was 1 °C/min). For kinetic studies, the catalyst powder samples were pressed into discs, crashed, and sieved to obtain catalyst particle sizes in the range of 250–500 μm. The Pt dispersion in the PtH-MFI catalyst was 12%. It was determined on a purpose-built adsorption system (Johnson Matthey) from the uptake of strongly chemisorbed CO at 25 °C and assuming CO/Pt adsorption ratio of 1. Prior to CO adsorption experiments the catalyst samples (0.5 g) were first oxidized at 530 °C for 4 h in flowing air (30 ml/min), and then reduced at 500 °C for 1 h in a flow of pure H_2 (30 ml/min).

2.2. Kinetic studies

Transformation of methane and benzene was studied at atmospheric pressure in a continuous flow reactor at 370 °C with the feed comprised of methane (90 mol%) and benzene (10 mol%). The reaction mixture was analyzed by on-line GC using Varian CP-3800 Gas Chromatograph, which was equipped with a molecular sieve 13X packed column and a thermal conductivity detector (TCD) for analysis of H_2, and a 25 m long PLOT Al_2O_3/KCl capillary column with a flame ionization detector (FID) for analysis of hydrocarbons (argon

was used as a carrier gas in both columns). TCD was calibrated using gas mixtures with different H_2 concentrations. Prior to the kinetic experiments, the catalyst samples were heated (1 °C/min) in the reactor under flowing air (30 ml/min) to 530 °C and kept at this temperature for 4 h. Then the temperature was reduced to 200 °C and the catalyst sample was purged with N_2 (50 ml/min) for 1 h before switching to the flowing H_2 (60 ml/min). The catalyst sample was then heated (5 °C/min) to 500 °C and kept at this temperature for 1 h before cooling the sample to the reaction temperature (370 °C).

Contact time (τ) was defined as WHSV^{-1}, where WHSV (h^{-1}) is the total weight hour space velocity of methane and benzene. Different levels of conversions of methane and benzene were obtained by performing experiments at different values of contact time. Time on stream experiments have shown steady-state operation of the catalyst between 4 and 23 h of the reaction, and the analysis of the reaction pathways was performed on the basis of the experimental data obtained at TOS between 4 and 6 h. To make sure that the oxidative methylation reaction [15] is not occurring in our catalytic system, we performed GC analysis of the feed mixture in every experiment. This analysis confirmed the absence of traces of oxygen and any other impurities in the feed up to a level of ~1 ppm.

3. Results and discussion

3.1. Time on stream experiments

Transformation of the mixture of methane and benzene over the PtH-MFI catalyst was studied in the continuous flow reactor at 370 °C during 23 h. Fig. 1 shows that conversions of benzene and methane were increasing during the first ~4 h of the reaction reaching 4.5% and 0.53% for benzene and methane, respectively. With further increase in TOS, a slow catalyst deactivation was observed.
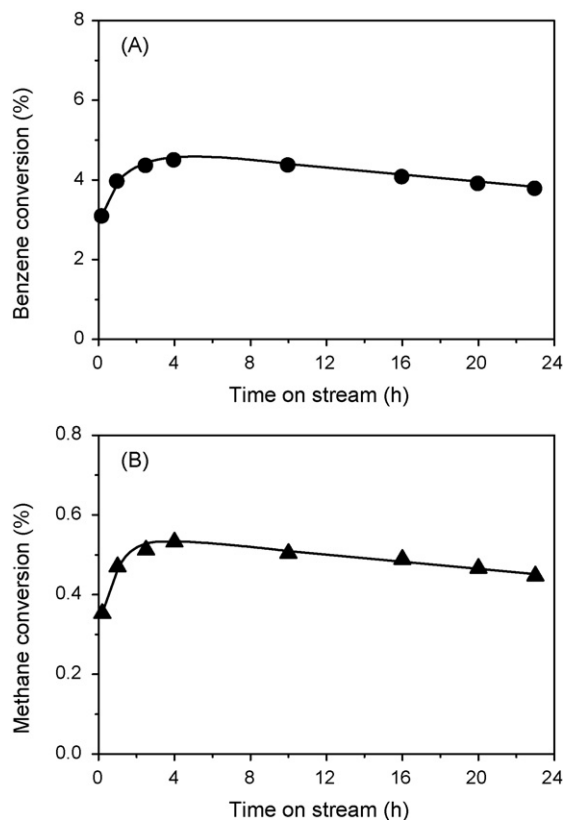

Fig. 1. Effect of time on stream on (A) benzene and (B) methane conversions over the PtH-MFI catalyst at 370 °C and WHSV of 1.76 h^{-1}. Methane to benzene molar ratio in the feed was 9:1.

Table 1
Selectivities to all carbon-containing products observed during methane and benzene reactions over the PtH-MFI catalyst at TOS of 4 h.

| Catalyst	PtH-MFI
Methane conversion (%)	0.53
Benzene conversion (%)	4.5
Selectivity (mol%)	
Ethane	2.7
Toluene	96.1
Ethylbenzene	0.15
Xylenes	1.05

Temperature = 370 °C; WHSV = 1.76 h^{-1}.

The major product of the reaction was toluene, which constituted 96.1 mol% of all carbon-containing products at TOS = 4 h (Table 1). Other carbon-containing products were produced in much smaller amounts and included ethane, EB and xylenes (Table 1). Ethane formation is important in principle, since it takes place also during transformation of pure methane on Pt/SiO$_2$ catalysts [21,25] and therefore reveals that methane is activated over the PtH-MFI catalyst under our reaction conditions. Taking into account the observed very high toluene selectivity, we can conclude that the activated methane reacts with benzene with selective formation of toluene. The extent of this reaction (Eq. (1)) is very significant, since the experimental conversions of benzene (4.5%) and methane (0.53%) at 4 h on stream are close to the equilibrium conversions: 5.6% and 0.62% for benzene and methane, respectively. The mode of toluene formation proposed above is different from the mechanism discussed by Kennedy et al. [16], who concluded that formation of toluene and other methylated products over H-beta zeolite proceed from benzene only. In our view, this difference is not surprising because of the different nature of the catalysts used in our and earlier [16] studies. In this connection, it is worth noting that formation of ethane was not observed during transformation of methane and benzene mixture over H-beta zeolite [16], thus indicating the absence of methane activation by this catalyst.

Let us now consider the initial (transient) period of methane and benzene reaction over the PtH-MFI catalyst (Fig. 1). In our opinion, the transient catalyst behavior during the first ~4 h on stream can be explained by the modification of the Pt particles with the surface carbonaceous species (e.g. CH$_3$, CH$_2$, CH, C, and C$_2$H$_x$). Formation of such surface species from methane on Pt particles, which was discussed by several research groups [19–28] for methane dissociative adsorption on different Group VIII transition metals, would lead to the development of the Pt active sites in working catalyst and, as a consequence, to the changes in the catalyst performance. In our case, as it follows from Fig. 1, we can assume that this modification is taking place during the first 4 h of the catalyst operation and leads to an increase in the catalyst activity. Formation of CH$_x$ surface species on Pt particles should lead to formation of H$_2$ in the gas phase, as schematically illustrated below by the reactions resulting in generation of the surface CH$_2$ and C (carbon or carbide) species:

$$CH_4 + [Pt] \rightarrow CH_2-[Pt] + H_2 \qquad (2)$$

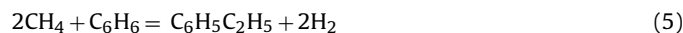$$CH_4 + [Pt] \rightarrow C-[Pt] + 2H_2 \qquad (3)$$

Hydrogen generated in reactions (2) and (3) cannot be related to formation of the products detected in the gas phase. Therefore, one would expect to observe hydrogen formation in excess of formation of the gaseous products, if our assumption on generation of the surface carbonaceous species is correct. The experimental data on hydrogen formation are presented in Fig. 2 and support fully this expectation. Indeed, Fig. 2 shows that the experimentally determined hydrogen concentration is significantly higher during the transient period than the hydrogen concentration, which corresponds to formation of the hydrocarbon products observed in the
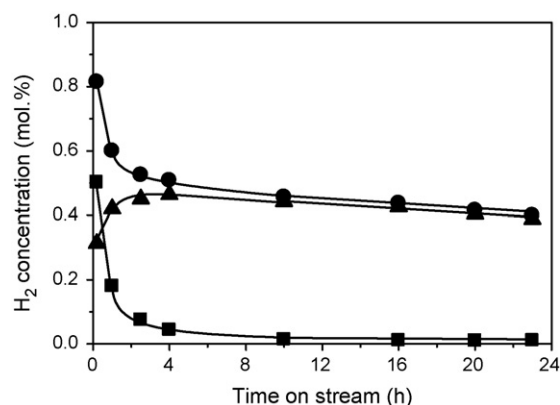

Fig. 2. Effect of time on stream on the concentration of hydrogen: (●) experimental values, (▲) calculated values, which correspond to formation of carbon-containing products observed in the gas phase, and (■) difference between the experimental and calculated values. Methane and benzene transformation was carried out over the PtH-MFI catalyst at 370 °C and WHSV of 1.76 h^{-1}. Methane to benzene molar ratio in the feed was 9:1.

gas phase. The latter was calculated on the basis of the experimentally determined concentrations of these hydrocarbon products (toluene, ethane, EB and xylenes) and the stoichiometric equations for reaction (1) and the reactions shown below:

$$2CH_4 = C_2H_6 + H_2 \qquad (4)$$

$$2CH_4 + C_6H_6 = C_6H_5C_2H_5 + 2H_2 \qquad (5)$$

$$2CH_4 + C_6H_6 = C_6H_4(CH_3)_2 + 2H_2 \qquad (6)$$

The difference between the experimental and calculated hydrogen concentrations is shown in Fig. 2 and corresponds to hydrogen released during formation of the surface carbonaceous species. Quite remarkably, this difference is decreasing rapidly during the first 4 h of the catalyst operation and then stabilizes at very low level (around 0.011 mol%). Such a pattern clearly indicates that two processes, which release H$_2$ in the gas phase, are taking place at the catalyst surface. The first process appears to be completed in about 4–6 h of the reaction (Fig. 2) and is likely responsible for the transient catalyst operation observed during this time period (Fig. 1). The second process is taking place during all 23 h of the experiment and produces H$_2$ in much smaller amounts than the first one (Fig. 2). Comparison of the data shown in Figs. 1 and 2 strongly suggests that this second process is associated with formation of inactive surface carbon-containing species (coke) that are responsible for the slow catalyst deactivation observed after 4–6 h on stream.

Fig. 3 shows the effect of time on stream on the selectivities of all carbon-containing products observed during methane and benzene transformations over the PtH-MFI catalyst at 370 °C. These data allow us to conclude that benzene alkylation with methane into toluene is the dominating reaction in our catalytic system during methane and benzene reactions in the course of 23 h. The highest toluene selectivity (98.6 mol%) was observed at TOS of 12 min, and then this selectivity decreased to 96.1 mol% at TOS = 4 h. Simultaneously, the selectivity to ethane increased from 0.68 mol% at TOS = 12 min to 2.7 mol% at TOS = 4 h. Importantly, the concentrations of both the toluene and ethane were increasing during this time period, but ethane concentration has increased by 6 times (from ~0.002 to 0.012 mol%) while the increase in toluene concentration was about 1.4 times (from 0.31 to 0.44 mol%). These results provide additional strong support to our assumption on the modification of the Pt active sites during the initial period of the reaction and indicate clearly that this modification leads to a stronger enhancement of ethane formation in comparison with formation of toluene. In our view, the observed different effects of the
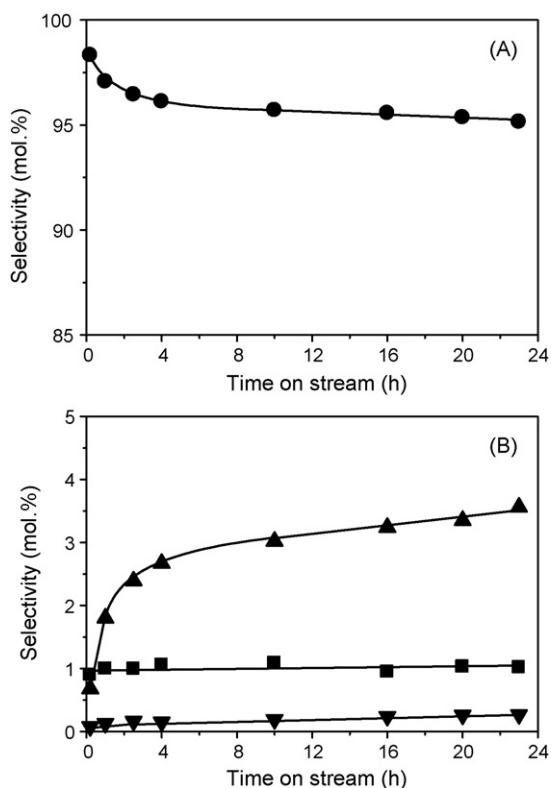
Fig. 3. Effect of time on stream on the selectivities to all carbon-containing products observed during methane and benzene transformation: (A) toluene (●); (B) ethane (▲), ethylbenzene (▼) and xylenes (■). The reaction was carried out over the PtH-MFI catalyst at 370 °C and WHSV of 1.76 h^{-1}. Methane to benzene molar ratio in the feed was 9:1.

Fig. 4. Concentrations of all observed reaction products as functions of methane conversion: (A) hydrogen (○) and toluene (●); (B) ethane (▲), ethylbenzene (▼) and xylenes (■). Methane and benzene transformation was carried out over the PtH-MFI catalyst at 370 °C, and methane to benzene molar ratio in the feed was 9:1. Methane conversion of 0.53% corresponds to benzene conversion of 4.5%.

surface carbonaceous species on formation of ethane and toluene are likely to be associated with the changes in the composition of these species with time. Indeed, it is reasonable to assume that CH$_x$ species, which are probably involved in formation of toluene and xylenes, are formed first on the Pt particles of the catalyst. As time progresses, more CH$_x$ species are formed and part of these species is transformed into C$_2$H$_x$ species (the possibility of such transformation is supported by the literature data [19–26]). These C$_2$H$_x$ species are likely to be transformed into ethane and to participate in benzene alkylation into ethylbenzene, which formation is enhanced with time in a similar way as formation of ethane (Fig. 3).

3.2. Pathways of methane and benzene transformations

To get better understanding of the pathways of methane and benzene transformations, we performed kinetic experiments at different contact times with the catalyst operating in the steady state (TOS was between 4 and 6 h). The results of these experiments are included in Fig. 4, which presents the product distributions as functions of methane conversion.

Fig. 4A reveals that hydrogen and toluene are the initial products of methane and benzene transformations and are likely to be produced via reaction (1). At the moment, the exact mechanism of this reaction is not clear. However, we believe that both the Brønsted acid and Pt sites are required for this reaction to proceed at relatively high rate. Our view is based on additional experiments, which were performed with the parent H-MFI zeolite and Pt/Al$_2$O$_3$ catalyst (these results will be reported in detail in a separate publication). In both cases formation of toluene was observed, but the toluene concentration was about 2–3 orders of magnitude lower than in the case of the PtH-MFI bifunctional catalyst, thus indicating that
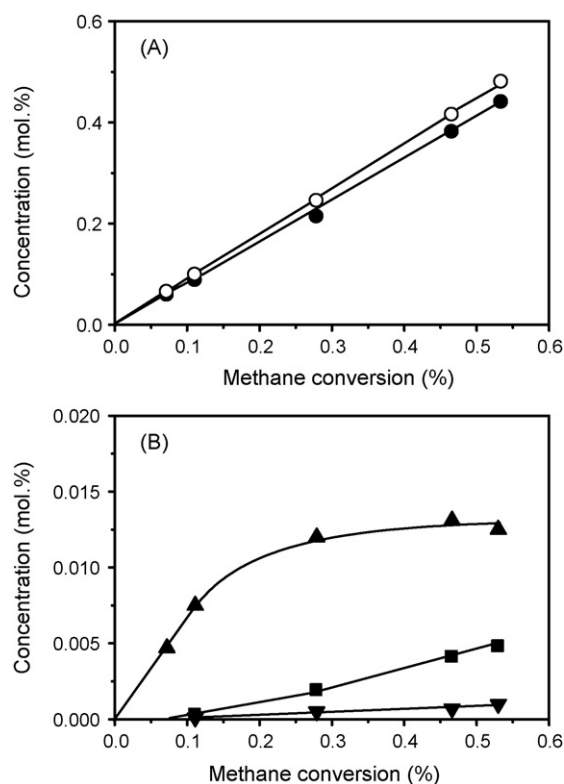
the presence of both the Brønsted acid and Pt sites in the catalyst is crucial for toluene formation.

Fig. 4B demonstrates that ethane is also formed as the initial product of the transformation of the mixture of methane and benzene over the PtH-MFI catalyst. Ethane is observed in much smaller quantities than hydrogen and toluene (note the difference between the scales in Fig. 4A and B), and its formation, as it follows from the literature [19–22,25], is possibly taking place in the reaction between two CH$_3$ species adsorbed on the Pt particles of the catalyst. From Fig. 4B it is clear that EB and xylenes are formed in the secondary reaction steps. Quite likely, EB is the product of the acid catalyzed benzene alkylation with ethene, which can be produced in very small concentrations via ethane dehydrogenation over Pt sites at 370 °C [17,18]. Formation of xylenes, in our view, is likely to proceed via toluene alkylation with methane in the similar way as formation of toluene from benzene and methane. Disproportionation of toluene over acid sites could be another reaction contributing to xylenes formation.

4. Conclusions

This paper demonstrates for the first time that methane reacts with benzene over bifunctional PtH-MFI catalyst with selective and stable formation of toluene at such low temperature as 370 °C. Our results show that the catalyst activity increases during the initial (transient) period of the reaction (~4 h). Analysis of the concentrations of H$_2$ and all carbon-containing products detected in the gas phase strongly suggests that this increase is likely to be associated with the modification of the Pt particles with the surface carbonaceous species (e.g. CH$_3$, CH$_2$, CH, C, and C$_2$H$_x$). Verification of this suggestion requires in situ spectroscopic characterization of these

species. The highest catalyst activity is observed at TOS of 4 h with conversions of benzene (4.5%) and methane (0.53%), which are close to the equilibrium values (5.6% and 0.62% for benzene and methane, respectively). At this time, the selectivity to toluene is 96.1 mol%, and the other carbon-containing products (ethane, ethylbenzene and xylenes) constitute the remaining 3.9 mol%. At higher TOS, the catalyst activity declines slowly and, at TOS of 23 h, conversions of benzene and methane are around 3.8% and 0.45%, respectively. During all 23 h of the reaction, the selectivity to toluene is staying above 95 mol%.

To the best of our knowledge, the reaction of benzene alkylation with methane into toluene, reported in this paper, is the first example of the catalytic reaction involving methane that proceeds continuously during many hours under non-oxidizing conditions. Therefore, we believe that our results open a new area for research into methane activation and transformation.

Acknowledgements

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