Dehydrogenation of methane on supported molybdenum oxides. Formation of benzene from methane

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The dehydrogenation of methane on MoO_3 supported on various oxides has been investigated under non-oxidizing conditions in a fixed bed, continuous flow reactor. Detailed measurements were performed with MoO_3/SiO_2. The reaction of methane was observed above 923 K after a significant time lag, when a partial reduction of Mo^{6+} occurred, the reduced phase being characterized by X-ray photoelectron spectroscopy (XPS). The initial gaseous products are CO_2, H_2O, H_2 and CO. But this stage is followed by the dehydrogenation of methane and coupling of hydrocarbon fragments to various hydrocarbons. A possible pathway of the formation of benzene, the main product of reaction with selectivities ranging from 26 to 56%, is suggested.

Keywords: methane; benzene; MoO_3/SiO_2

1. Introduction

Great effort is currently being made to convert methane into more valuable compounds. Most of the works to date dealt with the oxidative coupling of molecules of methane [1–3], with relatively little attention having been devoted to reaction of methane under non-oxidative conditions [4–11]. Studies in those areas show that the decomposition of methane to yield hydrogen on supported Pt metals occurs at relatively low temperature, typically 473 K, but the deposition of carbon poisons the active area leading to almost complete cessation of the decomposition [4–11]. Production of ethane has also been observed on supported Pt metals, very likely as a result of the coupling of the CH_3 species (the primary product of the CH_4 dissociation) and/or in the hydrogenation of surface carbon. In the present paper studies

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concerning the high temperature reaction of CH_4 with solid surfaces are extended to supported MoO_3 with particular attention to the effects of the support. A noteworthy paper has recently been published in this area by Wang et al. [12], who reported the dehydrogenation and aromatization of methane under non-oxidizing conditions on Mo- and Zn-modified ZSM-5 catalysts.

2. Experimental

2.1. METHODS

The reaction was carried out in a fixed-bed, continuous flow reactor. The reactor consisted of a quartz tube (20 mm i.d.), connected to a capillary tube (2 mm i.d.), so that the products could be rapidly removed from the hot zone. Generally 0.5 g of catalyst sample was used; and inlet gas consisted of methane with N_2 or He as diluent. The flow rate was usually 12 ml/min. Analysis of the exit gases was performed with a Chrompack CP 9001 gas chromatograph on Porapak P column. The methane conversion was calculated from the H_2 and H_2O balance. The selectivity values of product formation represent the fraction of methane that has been converted to the specific products taking account of the number of carbon atoms in the molecules.

A pulse reactor was also employed (8 mm o.d. quartz tube), which was incorporated between the sample inlet and the column of the gas chromatograph. In this case 0.3 g of sample was used.

The XPS measurements were performed in a Kratos XSAM 800 instrument at a base pressure of 10^{-8} Torr using Mg K_α primary radiation (14 kV, 15 mA). To compensate for possible charging effect, binding energies were normalized with respect to the position of the C(1s), this value being assumed constant at 284.6 eV. The pass energy was set at 40 eV; and an energy step width of 50 meV, and dwell time of 300 ms, were used. Typically 10 scans were accumulated for each spectrum. Fitting and deconvolution of the spectra were made using the VISION software (Kratos).

2.2. MATERIALS

The catalysts were prepared by impregnating the support with a basic solution of ammonium paramolybdate to yield a nominal 2 wt% of MoO_3. The following supports were used: Al_2O_3 (Degussa P 110 C1), TiO_2 (Degussa P25), SiO_2 (Cab-O-Sil), and MgO (DAB 6), NH_4ZSM-5 (Si/Al = 55.0). The suspension was dried at 373 K and calcined at 873 K for 5 h. Before the catalytic measurements, each sample was oxidized in an O_2 stream at 973 K in the reactor and then flushed with N_2 for 15 min.

The reactant gases CH_4 (99.995%), H_2 (99.95%) and O_2 (99.95%) were used as received. He (99.995%) and N_2 (99.995%) were purified with an oxy-trap. The other impurities were removed with the use of a 5A molecular sieve.

3. Results and discussion

The first part of our studies was concerned with the effects of supports on the reaction between CH_4 and MoO_3. As seen in fig. 1, methane interacts strongly with supported MoO_3 at 973 K. The reaction starts with a time lag, the length of which depends on the nature of the support, where there is only very little (0.1–0.6%) decomposition. After a short acceleration period the conversion attained a maximum value, which slowly decreased in time. The highest conversion of CH_4 ($\sim$ 5.4%) was reached for MoO_3/SiO_2, and the lowest (0.44%) for MoO_3/MgO.

H_2, CO and several higher hydrocarbons, C_2H_4, C_2H_6, C_3H_8, C_6H_6, C_7H_8, were identified among the products. The highest selectivity for benzene formation, 61% (taking into account only the carbon-containing gaseous products) was exhibited by MoO_3/H-ZSM5. The rates of the product formation measured for different samples at the maximum conversion and after 60 min reaction time are collected in table 1.

More detailed measurements were performed with the MoO_3/SiO_2 sample. Results for the effect of temperature are presented in fig. 2A. The lowest temperature, where the reaction of methane was detectable ($\sim$ 0.1% conversion), was 923 K. More extensive reaction of CH_4 occurs at 948 K after a time lag of 100 min. This value gradually decreases with increasing temperature.

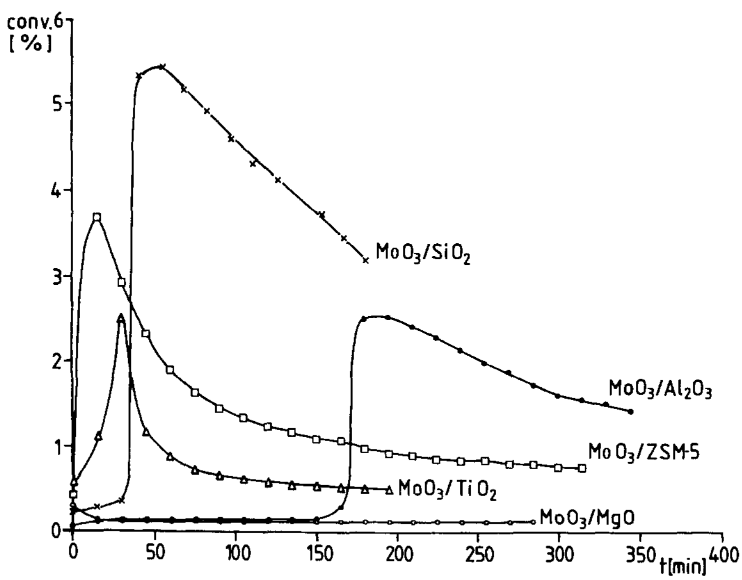

Fig. 1. Conversion of methane in the reaction with supported MoO_3 samples at 973 K.

Table 1
Some characteristic data for the oxidative conversion of CH_4 on supported MoO_3 catalysts at 973 K

	Time of reaction (min)	Conv. (%)	Formation rate (nmol/g s)							
			H_2	C_6H_6	CO	CO_2	C_2H_4	C_2H_6	C_3H_8	C_7H_8
MoO_3/SiO_2	60	5.44	1789	2.84	35.5	0	2.1	4.5	0.22	0.47
MoO_3/Al_2O_3	60	0.227	47.05	0	35	2	0.176	0.078	0.00	0.00
	195 [a]	2.53	812.8	3.47	179	0	4.43	4.07	0.118	0.089
MoO_3/TiO_2	60	0.886	284.5	0.441	62	0	3.81	0.50	0.094	0.018
	30 [a]	2.54	828	1.103	152	0	3.55	1.91	0.063	0.020
MoO_3/MgO	60	0.08	10.50	0	8	5	0	0.152	0.013	0
	1 [a]	0.44	44.03	0	49	23	0.217	1.586	0.012	0
MoO_3/HZSM-5	60	1.91	546.6	16.02	38	0	8.49	5.97	0.331	1.036
	15 [a]	3.68	1183.9	6.84	109	0	3.27	5.35	0.081	0.216

[a] Values determined at maximum conversion.

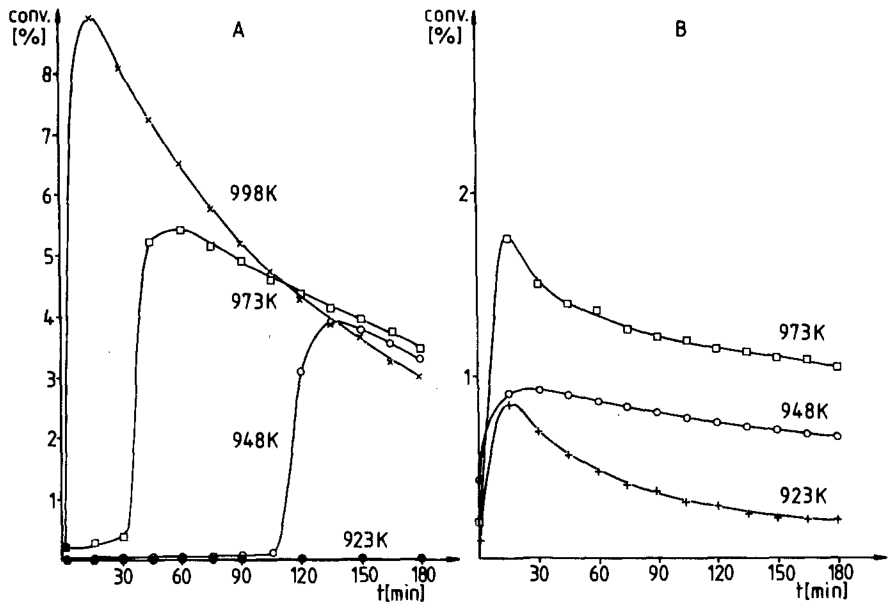

Fig. 2. (A) Effects of reaction temperature and (B) prereduction of MoO_3/SiO_2 catalyst at 973 K for 15 min on the conversion of methane decomposition at different temperatures.

Fig. 3 displays the product evolution at 973 K as a function of reaction time. The main ones at the initial phase of the interaction of CH_4 with MoO_3/SiO_2 are H_2, CO, H_2O and CO_2. Small amounts of ethylene, ethane and propane are also formed. The amount of carbonaceous species deposited during the induction period, up to 30 min, was 1050 μmol/g catalyst (determined by oxidation). The evolution of H_2 and CO dramatically increases after 30 min, when H_2O and CO_2 formation ceases. After attaining a maximum, the CO evolution drops sharply, whereas the H_2 evolution gradually decreases. Benzene and toluene appeared in the products at around 45 min, when the reaction of CH_4 became more extensive. Although the conversion of CH_4 slowly decayed after 60 min, the rates of benzene and toluene formation grew further as reaction ensued. As a result the selectivities for the production of these two compounds increased as a function of reaction time (fig. 4). The maximum value for the selectivity for benzene formation was 54.2%, if we take into account only the C-containing gaseous products. When H_2 was also considered as a product of CH_4 decomposition, this value was 4.7%. The amounts of other hydrocarbons decreased (C_2H_6), or remained practically constant (C_2H_4, C_3H_8) after the highest conversion of CH_4 decomposition (fig. 3). Selectivities for these hydrocarbons were constant or slightly decreased as a function of reaction time (fig. 4).

The product distribution was also affected by the reaction temperature. At 923 K, when the conversion of methane remained below 0.1% during several hours of reaction, we identified mainly the products of the reduction of MoO_3 (H_2O and

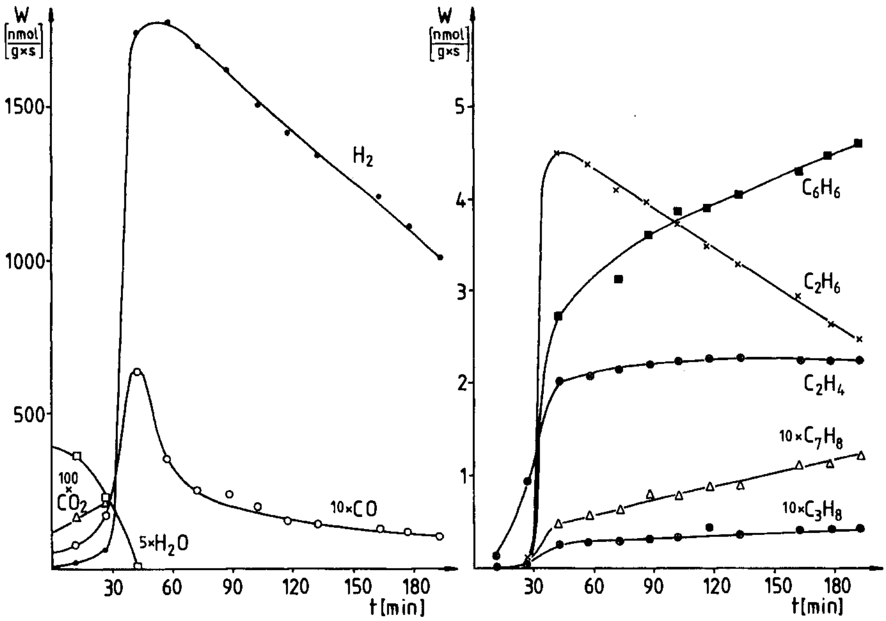

Fig. 3. Rate of formation of various products in the reaction of methane with MoO_3/SiO_2 at 973 K.

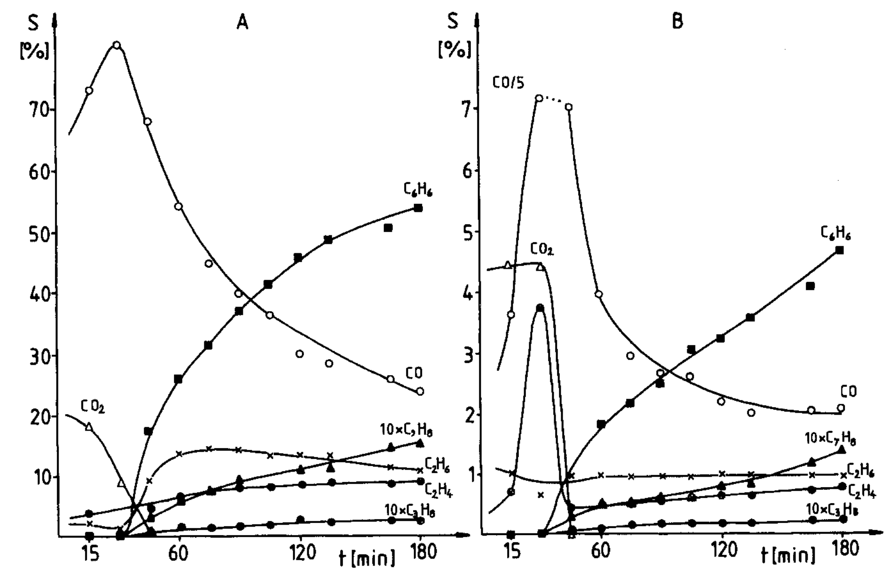

Fig. 4. Selectivities for various products formed in the reaction of methane with MoO_3/SiO_2 at 973 K. (A) with H_2, (B) without H_2.

CO_2). The formation of benzene occurred first at 948 K with maximum selectivities of 26.5% (without H_2) and 4.4% (with H_2). At higher temperatures, 998 K, these values were 52.4% and 13.1% respectively.

As regards the effects of various pretreatments on the induction period we found that pre-reduction of MoO_3/SiO_2 at 948–973 K shortened or eliminated the induction period altogether. This is demonstrated in fig. 2B. As a result of pre-reduction the decomposition of CH_4 and the formation of different hydrocarbons, including benzene, occurred even at 923 K, where otherwise the decomposition of CH_4 was below 0.1% even after several hours. The maximum conversion of CH_4 after pre-reduction was about 1.8% at 973 K. For the selectivity of benzene formation we obtained 59.0% (without H_2) and 13.5% after 180 min of reaction (with H_2).

These features suggest that a partial reduction of MoO_3 is required for the more extended conversion of CH_4, and particularly for the formation of benzene. From the amounts of H_2O and CO (+ CO_2) formed in the induction period at 973 K we calculated the extent of reduction during the induction period. We obtained that the average valency of Mo is around 4.0, which varied only slightly with the temperature between 948 and 993 K. Note that as a result of the high temperature treatment, the MoO_3/SiO_2 lost about 1.0% of its oxygen content before contacting with methane.

Further insight in the reduction was provided by XPS studies of the MoO_3/SiO_2 samples. The experimental and deconvoluted spectra for the catalysts before and after CH_4 treatment (40 min at 973 K) are displayed in fig. 5. In the deconvolution we followed the approach of Yang and Lunsford [13]. (i) The full width at half maximum (FWHM) of each peak in the doublets was assumed to be the same. (ii) The $3d_{5/2}$ and $3d_{3/2}$ binding energies were 232.1 and 235.3 eV for Mo^{6+}, 230.8 and 233.9 eV for Mo^{5+}, 229.8 and 233.0 eV for Mo^{4+}, 228.4 and 231.6 eV for Mo^{2+}, 227.6 and 230.8 eV for Mo^0. The values for Mo^{6+}–Mo^{4+} ions are almost the same as used by Yang and Lunsford [13]. The values for Mo^{2+} and Mo^0 are taken from the work of Hercules et al. [14]. Spectra presented in fig. 5 indicate that the oxidized sample contains a large excess of Mo^{6+} (84.4% Mo^{6+} and 15.6% Mo^{5+}). After a 40 min of reaction with CH_4 at 973 K, the intensity of the signal for Mo^{6+} is greatly decreased. The calculated composition is: Mo^{6+} (44.1%), Mo^{5+} (4.2%), Mo^{4+} (14.4%), Mo^{2+} (26.6%) and Mo^0 (10.5%).

In order to assist the evaluation of the mechanism of the formation of higher hydrocarbons and aromatics from methane, some measurements have been performed concerning the reactivity of carbon formed in the high temperature reaction. In the first experiment the MoO_3/SiO_2 catalyst was treated with CH_4 at 973 K for 40 min, then the catalyst bed was flushed with pure N_2 at 973 K. During the nitrogen flushing we detected only the evolution of methane and H_2. When N_2 was replaced with H_2 after 15 min, we found methane, ethane and benzene. The amount of benzene was only about 2.0% of that produced in the methane stream. When the catalyst was previously contacted with methane for a longer period, 180 min, the value of benzene was about one percent of that measured in the CH_4

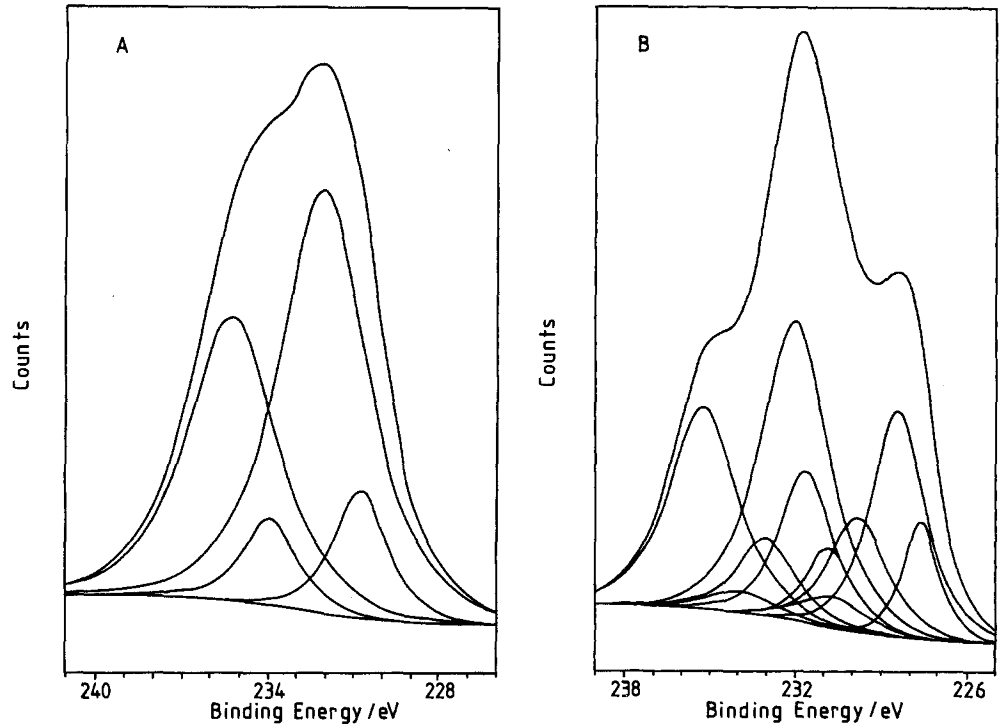

Fig. 5. XPS spectra of MoO_3/SiO_2 treated in different ways. (A) Calcined in O_2 flow at 973 K; (B) treated with methane at 973 K for 40 min.

stream before the interruption of the experiment. The formation of benzene in this case was detected even after 60 min. The reactivity of surface carbon towards hydrogen was also examined at lower temperatures. In this case, H_2 pulses (one pulse contained 36.1 μmol H_2) were admitted on the sample previously treated with methane at 973 K. The hydrogenation of carbon yielding methane was observed even at 373 K. Traces of C_2, C_3, and C_6 compounds were detected at 673 K. Calculation, however, showed that only an extremely small fraction (0.05–0.5%) of carbon deposited reacted with H_2 pulses at 373–673 K. All these results suggest that the carbonaceous species produced in the decomposition of methane at 973 K is very unreactive, and its hydrogenation contributes little, if at all, to the formation of higher hydrocarbons.

The results suggest that the reaction of methane with MoO_3/SiO_2 requires a rather high temperature. In the first stage of the reaction the reduction of MoO_3 proceeds to give CO (CO_2) and H_2O which can be described by the following overall equations:

$$3MoO_3 + CH_4 \rightleftharpoons CO + 2H_2O + 3MoO_2$$

$$4MoO_3 + CH_4 \rightleftharpoons CO_2 + 2H_2O + 4MoO_2$$

This reaction is followed by the dehydrogenation of CH_4 on practically reduced catalyst which could be an oxidative dehydrogenation process,

$$CH_4 + O_{(s)} \rightleftharpoons CH_3 + OH_{(s)}$$

$$2OH_{(s)} \rightleftharpoons H_2O + O_{(s)}$$

or a gradual decomposition of CH_4,

$$CH_4 \rightleftharpoons CH_3 + H$$

$$CH_3 \rightleftharpoons CH_2 + H$$

$$CH_2 \rightleftharpoons CH + H$$

$$2H \rightleftharpoons H_2$$

We may also count with the reaction of CH_4 with H_2O,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

which explains the steady formation of CO (fig. 3).

The fact that, besides H_2, saturated and unsaturated hydrocarbons are also formed, indicates the couplings of CH_x compounds,

$$2CH_3 \rightleftharpoons C_2H_6$$

$$2CH_2 \rightleftharpoons C_2H_4$$

$$C_2H_4 + CH_3 \rightleftharpoons C_3H_7$$

$$C_3H_7 + H \rightleftharpoons C_3H_8$$

These elementary steps have been observed on metal single crystal surfaces, at 100–300 K, when alkyl and alkene fragments have been produced in relatively high concentration by thermal and photo-dissociation of corresponding iodo compounds [15]. In the present case, however, the temperature is much higher. Taking into account the results and observations in the study of the oxidative coupling of methane to C_2 and higher hydrocarbons [1,2,16–18], it is very likely that the reactions of hydrocarbon fragments at 973 K occur mostly in the gas phase.

As regards the formation of benzene we mention that, thermodynamically, the dehydro-aromatization of methane is a more favorable reaction than dehydrodimerization [19]. We believe that the key compound in the formation of benzene is the ethane (formed in the coupling of two CH_3 radicals), which dehydrogenates to ethylene on the catalyst surface. This step is followed by dehydrogenative cyclization and aromatization of ethylene. It is an important observation that contacting ethane with MoO_3/SiO_2 catalyst at 973 K under the same conditions immediately produced benzene with 20% selectivity (based on C-containing materials). This reaction also requires high temperature, and a certain degree of the reduction of Mo^{6+}, as at lower temperature, 773–823 K, the reaction of ethane with MoO_3/SiO_2 gave only traces of CO, H_2O, CH_4 and C_2H_4. Note that in the presence of N_2O the oxidative dehydrogenation of ethane occurred at 773–823 K yielding acetaldehyde and ethylene [20,21].

4. Conclusions

(i) The reaction of methane with supported molybdenum oxides was observed above 923 K. The initial products are H_2O, CO, CO_2 and H_2.

(ii) The formation of hydrocarbons required the pre-reduction of Mo^{6+} at least to Mo^{4+}.

(iii) The main products of the oxidative conversion of methane on reduced MoO_3/SiO_2 sample is benzene with a highest selectivity of 56% at methane conversion of 3.2%.

Acknowledgement

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