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Efficient H_2 Production from Ethanol over Mo_2C/C Nanotube Catalyst

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Abstract Mo_2C deposited on silica is an effective catalyst for the decomposition of ethanol; the extent of the reaction approached 100% even at 623–673 K. Beside H_2 several C-containing compounds were produced, which caused the low yield of hydrogen. Preparation of Mo_2C by the reaction of MoO_3 with multiwall carbon nanotube, however, dramatically altered the product distribution. The formation of hydrogen came into prominence; about 40% of hydrogen content of ethanol decomposed at 523–723 K has been converted into H_2. Another feature of the Mo_2C/C nanotube is the relatively slow deactivation. Adding water to ethanol further enhanced the hydrogen production.

Keywords Hydrogen production · Ethanol decomposition · Mo_2C catalyst · Multiwall carbon nanotube as a support

1 Introduction

The production of hydrogen from alcohol, particularly from bioethanol gained an increasing attention in recent years [1–13]. Al_2O_3-supported noble metals are effective catalysts for the decomposition of ethanol, but the elimination of large amount of CO formed needed the use of gas mixture of ethanol + H_2O. Even in this case the reaction is operated at high temperatures around 973 K. Another drawback is the rapid deactivation of the catalysts very likely due to the deposition of strongly bonded acetate [14, 15]. In the light of these features, great efforts are being made: (i) to replace Pt metals with less expensive catalysts, (ii) to lower the reaction temperature, and (iii) to increase the stability of the catalyst.

Recently we found that the combination of Mo_2C with ZSM-5, which exhibited a unique catalytic performance in the direct conversion of methane and other alkanes into benzene [16–27], is an excellent catalyst for the aromatization of ethanol, too [28, 29]. High yield of aromatics (toluene, xylenes and benzene in decreasing selectivity) was obtained at 773–873 K. In this very complex process; beside the activation of ethanol, two reactions seemed important: the dehydration of ethanol to ethylene, and its subsequent dehydrocyclization to aromatics. In both processes the Brönsted acidic sites of ZSM-5 played an important role. The formation of H_2 was also registered during the reaction, but due to the production of several H-containing compounds (aromatics and other hydrocarbons) its amount was very low.

As will be demonstrated in this work the reaction pathway of ethanol can be dramatically altered, and the production of H_2 can be markedly enhanced by applying multiwall carbon nanotube as a support, which do not contain Brönsted sites important for the aromatization processes. The catalytic performance of Mo_2C/C nanotube is comparable with that of supported Pt metals.

2 Experimental

2.1 Methods

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm id) connected to a capillary tube [28, 29]. The

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flow rate was in general 40 mL/min. The carrier gas was Ar, which was bubbled through the ethanol at room temperature: its content was ~9.0%. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were analysed with two gas chromatographs: a HP 5890 equipped with PORAPAQ Q + S packed column (reaction of ethanol) and a HP 4890 equipped with PORAPAQ Q + S and 30-m long HP-PLOT Al_2O_3 column. In the study of the reaction of ethanol–water mixture of different composition, the reactants were introduced into an evaporator with the help of an infusion pump (MEDICOR ASSISTOR PCI flow rate : 1.0 mL liquid/h): the evaporator was flushed with Ar-flow (36 mL/min). Ethanol or ethanol–water containing Ar-flow entered the reactor through an externally heated tube avoiding condensation. The amount of surface carbonaceous deposit formed in the catalytic measurements was determined by temperature programmed reaction (TPR). After the reaction the sample was flushed with Ar at the reaction temperature and cooled down to 300–373 K. The sample was heated up with a 5 K/min heating rate in H_2 flow and the hydrocarbons formed were analyzed.

The conversion of ethanol was calculated taking into account its amount consumed. This value generally showed a good agreement with the those determined on the basis of H and C content of the reactant and products. To establish the efficiency of the catalyst as regards the production of hydrogen, the percentage of the H_2 related to the hydrogen content of ethanol decomposed was also calculated. This value is termed (named) as "H_2 yield".

XP spectra were taken with a Kratos XSAM 800 instrument using non-monochromatic Al K_α radiation ($h\nu$ = 1486.6 eV) and a 180° hemispherical analyzer at a base pressure of 1×10^{-9} mbar. Binding energies were referenced to the Fermi-level of the forming Mo_2C except for the initial stage of the experiments. For this state, the C 1s binding energy of carbon nanotube (285.1 eV) was accepted as reference.

2.2 Materials

Mo_2C/SiO_2 catalyst was prepared in the catalytic reactor by C_2H_6/H_2 [30]. The sample was heated under 10% v/v C_2H_6/H_2 gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min. Afterwards it was cooled down to room temperature under argon. The MoO_3/SiO_2 was produced by impregnating the silica with a basic solution of ammonium heptamolybdate to yield 2, 5 and 10 wt% of MoO_3. The suspension was dried and calcined at 863 K for 5 h.

Mo_2C on multiwall carbon nanotube (labelled as CNT) has been prepared in different way [31–33]. After impregnation of carbon into ammonium heptamolybdate, the dried suspension was treated in air at 673 K for 3 h. Afterwards the sample was heated in the catalytic reactor in H_2 flow up to 973 K with a temperature ramp of 3 K/min. Mo_2C/CNT was also prepared by using $MoCl_5$. The procedure is described by Pielaszek et al. [34]. The following materials were used as support. SiO_2 (Aerosil, 300 m^2/g), carbon nanotube (CNT) (170 m^2/g). The preparation carbon nanotube has been described elsewhere [35]. The gases used were of commercial purity (Linde).

3 Results and Discussion

3.1 XPS Measurements

Previous XPS studies showed that the carburization of MoO_3 deposited on silica by C_2H_6/H_2 mixture is complete using the method described in the Experimental Section [36, 37]. As very little known concerning the interaction of MoO_3 and Mo with carbon in the presence of hydrogen and on the production of Mo_2C in this system, it seemed inevitable to follow the reduction of MoO_3 on carbon nanotube and the formation of Mo_2C by XPS measurements.

XP spectrum of the MoO_3/CNT obtained after impregnation of carbon nanotube with $(NH_4)_2$ MoO_4 and pre-treated at 673 K in air shows the characteristic

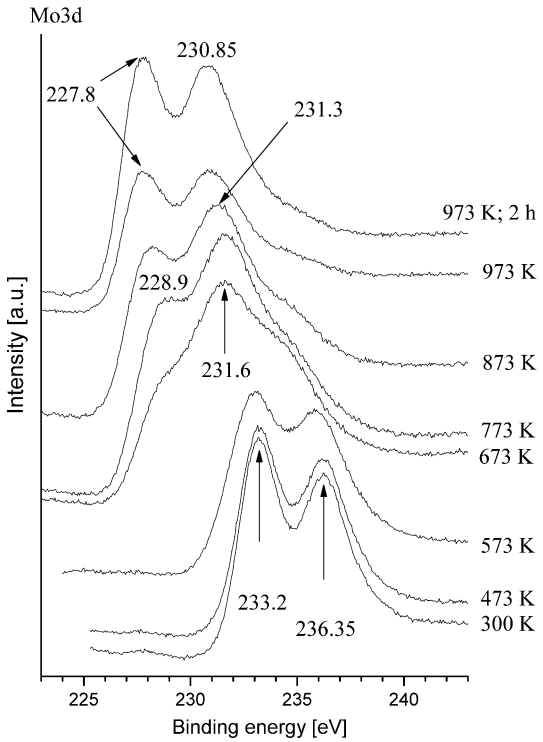

Fig. 1 XP spectra of MoO_3/CNT in the Mo region in the flow of hydrogen at different temperatures

$Mo3d_{3/2}$–$Mo3d_{5/2}$ doublet at 233.3 and 236.3 eV (Fig. 1). The O 1s binding energy was measured at 530.5 and 533.0 eV and that of C 1s at 285.1 eV. Heating the sample in H_2 flow (1 K/min) the first spectral changes were observed at 673 K due to the partial reduction of MoO_3. At 773 K the BE values for Mo appeared at 228.9 and 235.1 eV, which can be regarded as an indication of the presence of Mo_2C. The final values for the doublet, 227.8 and 230.9 eV measured at 973 K, agree well with those characteristic for Mo_2C [36, 37] suggesting that Mo reacted with carbon to give Mo_2C. In the course of this process a significant reduction in the intensity of O is peak occurred. Its complete elimination, however, was not achieved. The final value of C was registered at 284.9 eV. The shift from the initial value measured for carbon nanotube indicates that a new C-containing compound, namely Mo_2C, formed on the surface of carbon nanotube. For pure and unsupported Mo_2C this value was measured at 283.8 eV [36, 37].

3.2 Decomposition of Ethanol

First we examined the reaction of ethanol on silica supported Mo_2C prepared in situ, which possessed a high catalytic activity. Results obtained for 2% Mo_2C/SiO_2 are presented in Fig. 2. The decomposition was observed even at 473 K and a 90–95% conversion of ethanol was attainted at 723 K. The major products were hydrogen, water, ethylene, acetaldehyde, ethane and diethyl ether. Methane, CO and propene were formed only in few percents. The amount of H_2 was always less than that of ethylene at 623–823 K. The product distribution exhibited very little variation with the temperature. An exception is the diethyl ether: its amount gradually decreased from 623 K ($\sim$6%) to 0.3% at 823 K . The yield of H_2 (the amount of H_2 formed related to the hydrogen content of the ethanol decomposed) remained at low level, below 12% in the temperature range of 573–823 K. On increasing the Mo_2C content to 5 and 10 greatly enhanced the efficiency of the catalyst. On 10%Mo_2C/SiO_2 a conversion of 90–95% was attained even at 623 K resulting in the same kind of products as on the previous sample. The H_2 yield, however, did not exceed 15% even at 723 K.

Following the reaction in time on stream at this temperature we experienced a slow deactivation but the product distribution remained practically the same. Taking into account that only very small amounts of CO and CH_4 were produced in the temperature range of 573–723 K (Fig. 2), we may conclude that the reaction

$$C_2H_5OH = H_2 + CO + CH_4 \quad (1)$$

occurs only to a very small extent. The major reaction pathway on Mo_2C/SiO_2 is the dehydration of ethanol

$$C_2H_5OH = C_2H_4 + H_2O \quad (2)$$

to give ethylene, and the dehydrogenation

$$C_2H_5OH = CH_3CHO + H_2 \quad (3)$$

to yield acetaldehyde and hydrogen.

A completely different picture was obtained when Mo_2C was prepared on carbon nanotube, which does not contain acidic sites requited for the dehydrogenation of ethanol. On 5% Mo_2C/CNT, the decomposition of ethanol was also complete at 673–723 K (Fig. 3A). On this catalyst the formation of hydrogen drastically increased mainly at the expense of ethylene. The contribution of acetaldehyde to the products, however, remained practically the same as

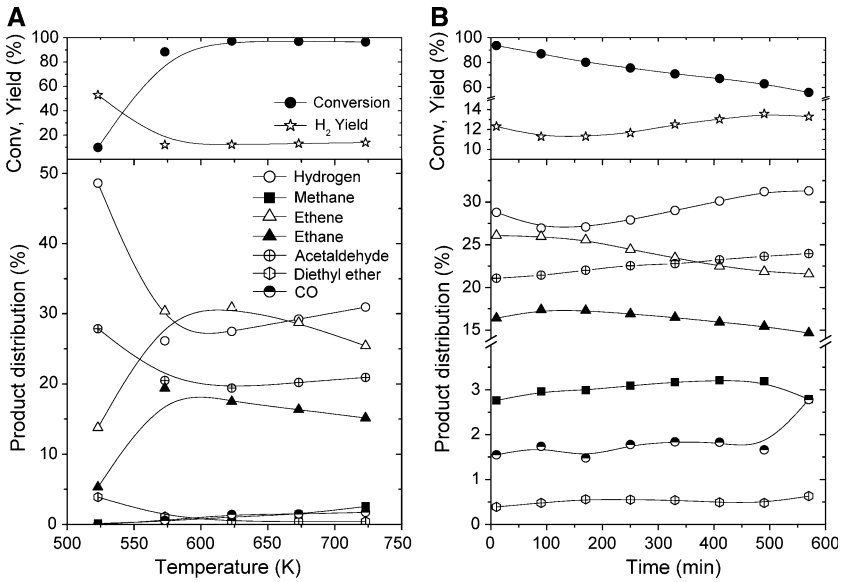

Fig. 2 Product distribution of the decomposition of ethanol on 10% Mo_2C/SiO_2 at different temperatures (**A**) and in time on stream at 723 K (**B**)

observed on Mo_2C/SiO_2. No CO and methane were detected below 623 K, but even above this temperature they formed only in few percents. Somewhat larger amount of ethane, maximum 5% at 673 K, was found. As a result of all these features the percentage of H_2 was much higher than that determined for Mo_2C/SiO_2 catalyst. Moreover, the yield of H_2 increased almost by a factor of 4, to ~40%. A slow decrease in the conversion of ethanol was measured in time on stream at 723 K, which only slightly influenced the product distribution (Fig. 3B).

In the subsequent measurements we examined the effect of water on the decomposition of ethanol over 5%Mo_2C/CNT catalyst. Characteristic data are displayed in Fig. 4. Addition of water to ethanol exerted no dramatic influence on the conversion of ethanol and on the product distribution, but increased clearly the percentage of hydrogen to ~75% and slightly decreased that of acetaldehyde and ethylene. This change can be attributed to the steam reforming of these compounds. The yield of H_2 approached the value of 50% or more. As shown in Fig. 4B the catalyst underwent only slow deterioration in ~9 h at 723 K without altering the product distribution.

As regards the activation of ethanol we propose the following consideration. Based on the previous studies [38–43], we assume that carbon deficient sites on the Mo_2C surface are the active centers of the catalyst. The first step of the reaction is very likely the dissociation of ethanol to ethoxy species, which is bonded with its oxygen end to the active sites of Mo_2C [28, 29]. The deactivation of the catalyst may be ascribed to the deposition of carbon and

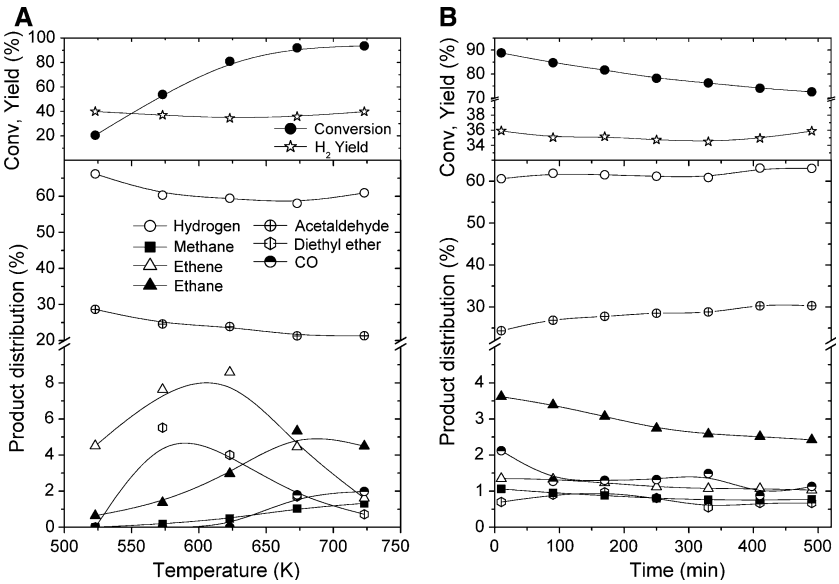

Fig. 3 Product distribution of the decomposition of ethanol on 5% Mo_2C/CNT at different temperatures (**A**) and in time on stream at 723 K (**B**)

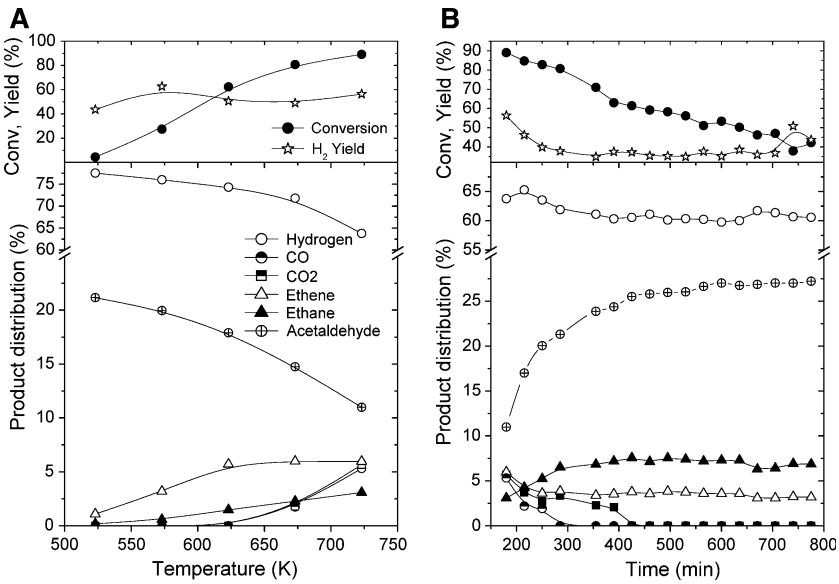

Fig. 4 Effects of water on the product distribution of ethanol decomposition on 5% Mo_2C/CNT at different temperatures (**A**) and in time on stream at 723 K (**B**) The ratio of ethanol:water was 1:3

oxygen on these centers formed in the complete disintegration of ethanol and/or its products, for example CO [41, 42]. The fact, however, is that we experienced relatively slow deactivation, may indicate that the hydrogen formed in the decomposition can react with this carbon and oxygen species thereby regenerating the active sites. XPS studies performed in a reactor combined with the XPS system showed no enhancement of O (1s) signal of the used catalyst (5h reaction at 723 K) as compared to the value measured for the starting sample. Alternatively, the carbon may diffuse from the Mo_2C onto the nanotube surface.

In order to obtain a deeper insight in the steps occurring on Mo_2C surface, the interaction of ethanol, ethylene and acetaldehyde with Mo_2C/Mo(100) is undertaken in UHV using various electron spectroscopic methods.

4 Conclusions

(i) Mo_2C deposited on silica is an active catalyst for the decomposition of ethanol to give hydrogen and several hydrocarbons. The extent of the ethanol decomposition was almost 100% above 623–673 K.

(ii) A dramatic increase in the production of hydrogen was achieved when Mo_2C was prepared by the reaction of MoO_3 with carbon nanotube. At complete decomposition of ethanol 35–40% of the H_2 content of ethanol has been converted into H_2.

(iii) This value increased to 55–60% using $C_2H_5OH + H_2O$ mixture.

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