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# The decomposition of ethanol over $Mo_2C$/carbon catalysts

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## Abstract

The formation of $Mo_2C$ by the reaction of $MoO_3$ with carbon Norit in $H_2$ flow was followed by X-ray photoelectron spectroscopy. It was found that the conversion of $MoO_3$ into $Mo_2C$ in the surface layer of Norit was complete at 973 K. $Mo_2C$ prepared in this way on the surface of carbon Norit was found to be an effective catalyst for the decomposition of ethanol to generate $H_2$; the extent of the reaction approached 100% even at 623–673 K. Depending on the temperature and the $Mo_2C$ loading about 32–62% of hydrogen content of the decomposed ethanol has been converted into $H_2$. Besides $H_2$, acetaldehyde was the major product indicating that the dehydrogenation reaction of ethanol is the main process. The formation of $CH_4$, CO, $C_2H_4$ and $C_2H_6$ also occurred in few percents. Another feature of the $Mo_2C$/Norit catalysts is its high stability. The conversion of ethanol decreased only with few percent even after 75 h at 723 K. Adding potassium to $Mo_2C$/Norit enhanced the catalytic efficiency of $Mo_2C$ and increased the formation of hydrogen. $Mo_2C$ prepared on multiwall carbon nanotube also proved to be active for the decomposition of ethanol. Adding water to ethanol enhanced the hydrogen production only to a small extent.

*Keywords:* Hydrogen production; Ethanol decomposition; Preparation of $Mo_2C$ on Norit; $Mo_2C$ on carbon nanotube; X-ray photoelectron spectroscopy; $Mo_2C$ catalyst; Carbon as a support

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## 1. Introduction

The demand of clean hydrogen for rapid developments of fuel cell initiated a tremendous interest in producing hydrogen [1–3]. Direct decomposition of methane seems an attractive route for production of CO/$CO_2$-free hydrogen, which is effectively catalyzed by supported Pt metals [4–10]. The deposition of carbon on the catalysts, however, leads to early deactivation, and the regeneration of catalyst makes this method less attractive. Ethanol is also considered as a new raw material, which depending on the nature of catalyst, can be converted into hydrocarbons, even in aromatics [11–16], or into hydrogen with a high yield [17–29]. Extensive studies have been carried out to find an efficient, stable and cheap catalyst for the latter process. As in other reactions, $Al_2O_3$-supported Pt metals are active materials for the decomposition of ethanol to yield hydrogen, but neither of them fulfill the above requirements. Besides, the formation of large amount of CO required the use of a mixture of $C_2H_5OH + H_2O$. Even in this case the reaction is operated at high temperatures, around 873–973 K. Another drawback is the rapid deactivation of many catalysts very likely due to the deposition of strongly bonded acetate [30,31]. In the light of these features, great efforts are being made: (i) to replace Pt metals with less expensive materials, (ii) to lower the reaction temperature, and (iii) to increase the stability of the catalyst. The synthesis and search for new catalysts is really needed. One of the candidates is $Mo_2C$, which exhibited favorable catalytic performance in several reactions, such as water-gas-shift-reaction, hydrodesulfurization, hydrodenitrogenation, dehydrogenation and hydrogenation processes, [32,33]. Its combination with ZSM-5 exhibited a unique catalytic performance in the direct conversion of methane and other alkanes into benzene [34–45]. The $Mo_2C$/ZSM-5 proved to be an excellent catalyst for the aromatization of ethanol, too [46,47].

In a short preliminary communication we reported that the reaction pathway of ethanol on $Mo_2C$ can be dramatically altered, and the production of $H_2$ can be markedly enhanced by applying multiwall carbon nanotube as a support [48]. In this paper we examine the catalytic behavior of $Mo_2C$ prepared on

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carbon Norit in the decomposition and steam reforming of ethanol, and present some new results for $Mo_2C$ deposited on multiwall carbon nanotube.

## 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 i.d.) connected to a capillary tube [46,47]. The flow rate was varied between 12 and 400 mL/min, but in general it was 40 mL/min. The carrier gas was Ar, which was saturated with ethanol at room temperature: its content was ~9.0%. Reaction products were analyzed with two gas chromatographs: a HP 5890 equipped with PORAPAQ Q + S packed column 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 conversion of ethanol was mainly calculated taking into account its amount consumed. In certain cases it was also determined on the basis of H and C content of the reactant and products.

Hydrogen and different product selectivities were defined as

$$S_{H_2} = \frac{x_{H_2}}{\sum x_i n_i}, \qquad S_i = \frac{x_i n_i}{\sum x_i n_i}$$

where $x_i$ and $x_{H_2}$ are the mole fractions of product (i) and $H_2$, respectively, and $n_i$ is half of the number of hydrogen atoms (in the calculation of $S_{H_2}$), of the number of carbon atoms (in the calculation of $S_i$) in each molecule of product (i). 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 as "$H_2$ yield".

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 ~ 373 K. The sample was heated up with a 5 K/min heating rate in $H_2$ flow and the hydrocarbons formed were analyzed. Thermal desorption measurements (TPD) were carried out in the catalytic reactor. The $Mo_2C$/Norit sample was treated with $C_2H_5OH$/Ar gas mixture at 348 K for 30 min. Afterward the sample was flushed with Ar for 30 min at 348 K, then heated gradually in argon (5 K/min) and the desorbing products were analysed by gas chromatograph.

The dispersion of $Mo_2C$/Norit has been determined on in situ prepared samples by CO pulses in the reactor after cooling the catalysts in Ar flow to ~310 K. Data are collected in Table 1. XP spectra were taken with a Kratos XSAM 800 instrument using non-monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV) and a 180° hemispherical analyzer at a base pressure of $1 \times 10^{-9}$ 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 Norit (285.1 eV) was accepted as reference.

Table 1
Adsorption of CO on $Mo_2C$ catalysts at 300 K

| Catalyst | CO uptake μmol/g catalyst |
|---|---|
| 1% $Mo_2C$/Norit | 12.4 |
| 5% $Mo_2C$/Norit | 26.1 |
| 10% $Mo_2C$/Norit | 39.4 |
| 1% $Mo_2C$/CNT | 3.6 |
| 10% $Mo_2C$/CNT | 8.9 |

### 2.2. Materials

The following materials were used as supports. Multiwall carbon nanotube (labelled as CNT) and activated carbon Norit, ROW 0.8 mm pellets (labelled as Norit). The surface area of CNT is 170 $m^2$/g, and that of Norit 1175 $m^2$/g. The preparation and purification of carbon nanotube has been described elsewhere [49]. Carbon Norit was purchased from ALFA AESAR. It has been purified by treating it with HCl (~10%) for 12 h at room temperature. After this treatment the metal impurities, mainly iron, were less than 0.02% determined by ICP–AES method. Supported $Mo_2C$ has been prepared by impregnation of carbon into ammonium heptamolybdate solution to yield 1, 5 and 10 wt.% of $MoO_3$. For the preparation of K-promoted $Mo_2C$, carbon Norit was impregnated in the solution of $K_2MoO_4$. Further treatment was the same as in the case of undoped sample. This sample contained 2.7% K and 7% $Mo_2C$. The dried suspension was calcined in air at 673 K for 3 h. Instead of the carburization of $MoO_3$ it was heated in the catalytic reactor in $H_2$ flow up to 973 K with a temperature ramp of 3 K/min. Previous XRD studies revealed that the partially reduced $MoO_3$ reacts with carbon to give β-$Mo_2C$ [50,51]. The amount of the catalyst used was 0.3 g. Ethanol was the product of SPEKTRUM-3D with purity of 99.7%.

## 3. Results

### 3.1. Reaction of $MoO_3$ with carbon, XPS measurements

The reaction of $MoO_3$ with carbon Norit, e.g. the formation of $Mo_2C$ has been followed by XPS. XP spectrum of the $MoO_3$/Norit shows the characteristic Mo $3d_{3/2}$–Mo$3d_{5/2}$ doublet at 233.1 and 236.2 eV (Fig. 1). The O 1s binding energy (BE) was measured at 530.7 eV and that of C 1s at 285.1 eV. Heating the sample in $H_2$ flow (3 K/min) the first spectral changes were observed at 573 K due to the partial reduction of $MoO_3$. At 773 K the BE values for Mo appeared at 228.2 and 232.1 eV, which can be regarded as an indication of the presence of $Mo_2C$. The final values for the doublet, 227.8 and 231.0 eV measured at 973 K, agree well with those characteristic for $Mo_2C$ [52,53] suggesting that Mo reacted with carbon to give $Mo_2C$. In the course of this process a significant reduction in the