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THERMAL CHARACTERISATION OF MOLYBDENUM AND PLATINUM-MOLYBDENUM CATALYSTS

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Alumina supported Mo and Pt-Mo catalysts was subject to temperature programmed reduction (TPR) using H_2 and CO. After earlier oxidation step TPR–H_2 profiles shows different surface species, which depends on the composition of the catalysts and reduction temperature. Change in reducing gas from H_2 into CO results in significant changes in catalyst system. Hydrogen causes a decrease in oxidation number of metals, while carbon monoxide reacts with chemisorbed chemicals.

Keywords: *Mo/Al_2O_3, Pt-Mo/Al_2O_3 catalysts, TPR–CO, TPR–H_2*

Introduction

The catalysts containing platinum or platinum and molybdenum supported on alumina or other supports and obtained by different methods of preparation have been studied by many authors [1–11]. Usually one of the components of such catalysts is platinum at a low concentration, while the second component are metal ions applied mainly to reduce the price of the catalysts without changes in their efficiency and selectivity. Bimetallic catalysts Pt-Mo/Al_2O_3 have been used in a number of reactions such as hydrogenation, dehydrogenation, hydrogenolysis and isomerisation [1–5] and synthesis of alcohols from CO and H_2 [6] and in combustion of methane [7]. Because of this wide scope of their application the catalysts have been studied by many authors. Of great interest is the recognition of the catalysts structure and mutual interactions of their components in the process of reduction. The knowledge of these phenomena would be essential for designing catalysts of high activity and selectivity. One of the effective methods of the catalysts study has proved to be the temperature programmed reduction (TPR) [13]. In this method the effects of reducing the oxide species of the catalysts components appearing with a linear increase in temperature are recorded in the form of peaks corresponding to the use of the reducing gas. The positions of the peaks are related to the energy of activation of the reduction processes. On the basis of the number of peaks and their positions it is possible to conclude about the texture of the catalyst surface, which is important in design of catalysts synthesis and their regeneration.

Experimental

The catalysts were prepared by the impregnation of the pores in γ-Al_2O_3 (Degussa C) by the incipient wetness method with aqueous solutions of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}$] and chloroplatinic acid (H_2PtCl_6) according to the earlier described procedure [8]. The preparations obtained were subjected to calcination and oxidation.

The temperature programmed reduction (TPR) measurements were performed on an AMI I instrument with a katarometer as a detector when hydrogen was used for reduction (5% H_2/95%Ar) or a quadrupole mass spectrophotometer made by Dycor – in reduction with carbon oxide (5% CO/95% Ar). Two series of measurements were made. The samples studied in the first series were at first calcined for 5 h at 500°C and oxidised with oxygen (5% O_2/95% Ar) at T_u (°C) and then subjected to the process of TPR-H_2. The samples studied in the second series were at first subjected to oxidation at 500°C then to TPR–CO at 700°C at the gas flow rate of 40 $cm^3 min^{-1}$ and the temperature increase rate of 15°C min^{-1}. On oxidation the sample of 200 mg was heated to a desired temperature maintained for 30 min, while on TPR–CO the measurements were made after 10 min.

Results and discussion

The TPR measurements were performed for the catalysts given in Table 1.

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Table 1 Nomenclature, nominal composition and surface area of catalysts

Catalysts	Surface area/$m^2\ g^{-1}$
Al_2O_3 Degussa C	93
$0.3^{\#}$ Pt/Al_2O_3	93
$2Mo/Al_2O_3$	93
$20Mo/Al_2O_3$	69
$0.3Pt–2Mo/Al_2O_3$	95
$0.3Pt–20Mo/Al_2O_3$	77

$^{\#}$mass%

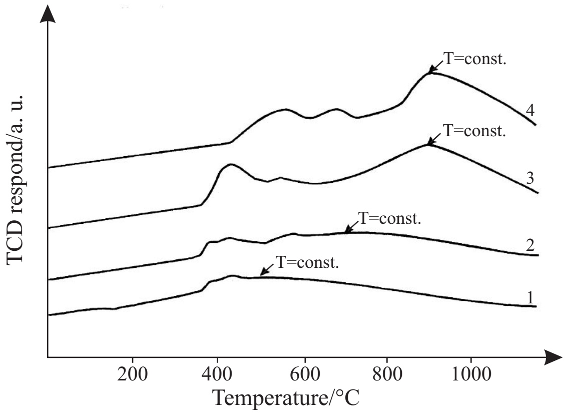

Fig. 1 TPR–H_2 profiles recorded for the catalyst containing $2Mo/Al_2O_3$ after oxidation at different temperatures

Figures 1–4 present the TPR–H_2 profiles of the catalysts containing molybdenum (Figs 1 and 3) and platinum and molybdenum (Figs 2 and 4). Each figure shows four profiles recorded in the following conditions:

1 – T_u=400°C, TPR–H_2=500°C
2 – T_u=500°C, TPR–H_2=700°C
3 – T_u=700°C, TPR–H_2=900°C
4 – T_u=900°C, TPR–H_2=900°C

Figure 1 shows the profiles obtained for the samples $2Mo/Al_2O_3$ subjected to oxidation at different temperatures (T_u) and then to TPR–H_2. The reduction of these samples occurs in the whole temperature range studied. The peaks corresponding to enhanced consumption of hydrogen occur at 400 and 440°C (curves 1 and 2) and another one at about 600°C. If the sample is subjected to oxidation at 700°C then the TPR profile (curve 3) shows a considerable consumption of hydrogen at 430, 560 and 900°C. The oxidation at 900°C followed by TPR–H_2 (curve 4) give the profile with three peaks at 570, 690 and 900°C.

The profiles of the catalysts containing 0.3Pt–2Mo oxidized at 400 and 500°C (curves 1 and 2) and subjected to TPR–H_2 reveal two small and broadened peaks at 500 and 700°C. Curve 1 shows two well pronounced thermal effects related to the reduction of Pt–Mo surface groups, the analogous effects in curve 2 are much smaller and accompanied by the third effect at about 700°C this means that as a result of oxidation and reduction in higher temperatures of 500 and 700°C, respectively, the third type of Pt–Mo species susceptible to reduction appears. Curve 3 recorded for the sample after oxidation at 700°C and then reduction in temperatures up to 900°C, shows two well marked effects corresponding to the peaks at 530 and 900°C. Similarly, two maxima appear for the sample oxidized at 900°C and then subjected to TPR–H_2.

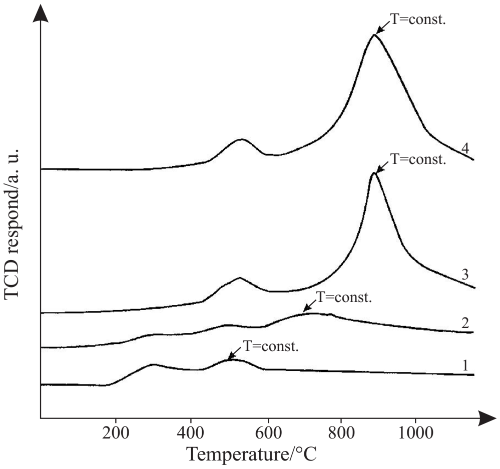

Fig. 2 TPR–H_2 profiles for the sample containing $0.3Pt–2Mo/Al_2O_3$ after oxidation at two different tem-

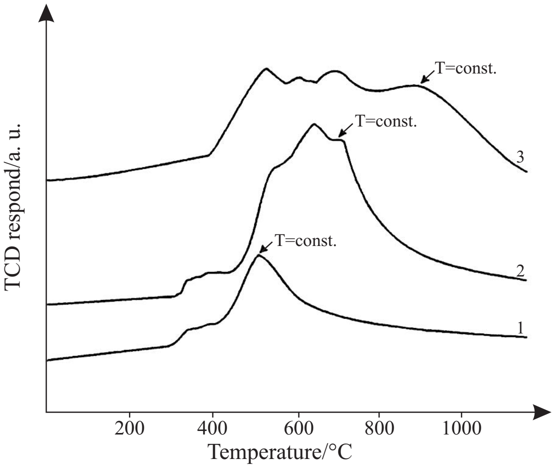

Fig. 3 TPR–H_2 profiles of the sample $20Mo/Al_2O_3$ after oxidation at different temperatures

A comparison of the TPR–H_2 profiles recorded for the samples with $2Mo/Al_2O_3$ and $0.3Pt–2Mo/Al_2O_3$ has shown that in the samples subjected to oxidation at 400 and 500°C (Fig. 1, curves 1

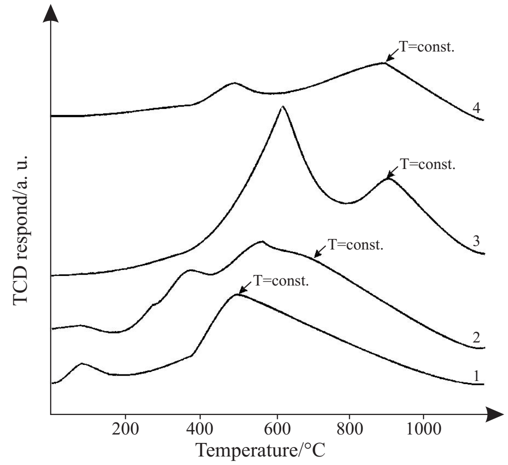

Fig. 4 TPR–H_2 profiles of the catalysts 0.3Pt–20Mo/Al_2O_3 after preliminary oxidation at different temperatures

and 2) there are two (the first sample) and three (the second sample) molybdenum species.

The addition of platinum results in the appearance of new Pt–Mo surface species (Fig. 2, curves 1 and 2), undergoing reduction at different temperatures. In the samples oxidised at 700 and 900°C, their reduction causes an enhanced consumption of hydrogen (Figs 1 and 2, curves 3 and 4). However, in the samples with platinum (Fig. 2) the hydrogen consumption is much greater, which means that in these conditions two different Pt–Mo species are formed in large amounts.

Figures 3 and 4 present the TPR–H_2 profiles of the samples with 20Mo/Al_2O_3 and 0.3Pt–20Mo/Al_2O_3. In the samples oxidized at 400°C and then reduced (Figs 3 and 4, curve 1) an addition of platinum causes a significant decrease in the temperature of the molybdenum species reduction assigned to a small double peak with the maxima at 330 and 400°C (Fig. 3, curve 1) to 90°C (Fig. 4, curve 1) which can be related to the appearance of Pt–Mo species. An increase in the oxidation temperature of the sample with molybdenum to 500°C (Fig. 3, curve 3) results in a small effect in the range 340–400°C and a large effect in the range 460–700°C, marked with a triple peak. This peak indicates the presence of three surface molybdenum species of similar structure. Introduction of platinum into the sample with 20Mo/Al_2O_3 (Fig. 4, curve 2) shifts the peaks corresponding to the maxima of hydrogen consumption towards lower temperatures relative to the positions of the peaks recorded for the sample without platinum.

Curve 3 of Fig. 2 recorded for the sample 0.3Pt–2Mo/Al_2O_3 oxidized at 700°C and then subjected to reduction up to 900°C shows two great effects, one at about 530°C and the other at 900°C. Similar two peaks are observed for the sample (Fig. 2, curve 4) oxidized at 900°C and then subjected to TPR–H_2. The TPR–H_2 profiles of the samples without platinum 2Mo/Al_2O_3 oxidized at 400 and 500°C (Fig. 1, curves 1 and 2) reveal the presence of two and three molybdenum species, respectively. The addition of platinum to get 0.3Pt–2Mo/Al_2O_3 causes the formation of new surface Pt–Mo groups (Fig. 2, curves 1 and 2), which undergo reduction in different temperatures.

In the samples oxidized at higher temperatures (700 and 900°C) the reduction causes an enhanced consumption of hydrogen (Figs 1 and 2, curves 3 and 4), but for the samples with platinum (Fig. 2) the hydrogen consumption is much greater. It means the formation of large amounts of two different Pt–Mo species.

Figures 3 and 4 present the TPR–H_2 profiles recorded for the samples 20Mo/Al_2O_3 and 0.3Pt–20Mo/Al_2O_3. In the samples oxidized at 400°C and then reduced (Figs 3 and 4, curve 1), the addition of platinum causes a significant decrease in the temperature of reduction of the molybdenum species corresponding to the small double peak with the maxima at 330 and 400–900°C (Fig. 4, curve 1), which can be related to formation of a Pt–Mo species. The oxidation of the sample without platinum at 500°C (Fig. 3, curve 3) causes a small effect in the range 340–400°C and a large effect in the range 460–700°C, corresponding to the triple peak. This peak is interpreted as indicating the presence of three molybdenum species of similar structure. The TPR–H_2 profile of the sample oxidized at 700°C and then subjected to reduction shows a number of relatively small peaks (Fig. 3, curve 3) at 540, 620, 710 and 900°C. In the profile of the sample 0.3Pt–20Mo/Al_2O_3 the first three of the above peaks become a single peak occurring at 630°C (Fig. 4, curve 3). The profile of the sample with platinum oxidized at 900°C and then subjected to TPR–H_2 shows two peaks with the maxima at 500 and 900°C (Fig. 4, curve 4).

An increase in the molybdenum concentration on the surface of Al_2O_3 from 2 to 20 mass%. (Figs 1 and 2) results in significant changes in the hydrogen consumption peak positions, that is their shift towards higher temperatures. For the samples containing 0.3 mass% Pt, an increase in the molybdenum concentration from 2 to 20 mass% (Figs 2 and 4) does not cause the unidirectional changes, some peaks are shifted towards higher and some to lower temperatures.

The use of hydrogen in TPR to reduce the oxide catalysts causes a decrease in the oxidation degree of the metal cation and the liberation of water.

If another reducing agent is used, e.g. carbon oxide, then the reduction of the oxidation degree can be accompanied by some reactions. Figure 5 presents the profiles recorded for the samples 2Mo/Al_2O_3 and 0.3Pt–Mo/Al_2O_3 oxidized at 500°C and then reduced by carbon oxide at 700°C. The reaction products are methane, hydrogen and carbon dioxide, so over the

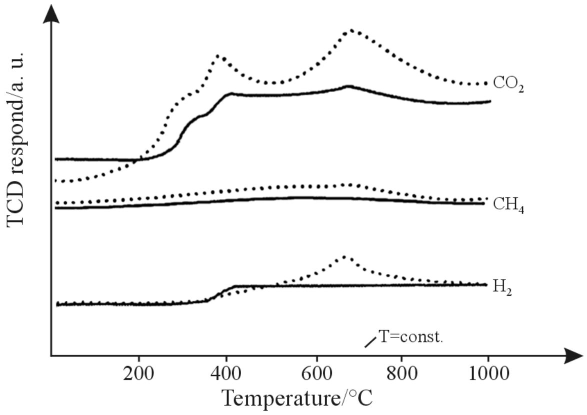

Fig. 5 TPR–CO profiles recorded for the catalysts — – $2Mo/Al_2O_3$ and ··· – $0.3Pt–2Mo/Al_2O_3$

catalysts applied carbon oxide can undergo reduction to methane according to the reaction:

$$CO+3H_2 \rightarrow CH_4+H_2O \qquad (1)$$

The water formed in the reaction can be involved in the following catalytic reactions:

$$CO+H_2O \rightarrow CO_2+H_2 \qquad (2)$$

$$CH_4+H_2O \rightarrow CO+3H_2 \qquad (3)$$

The oxidation of the sample without platinum at 500°C (Fig. 3, curve 3) causes a small effect in the range 340–400°C and a large effect in the range 460–700°C, corresponding to the Analysis of the data presented in Fig. 5 implies that the amount of methane produced in the reaction over the catalyst Mo/Al_2O_3 is small. Nevertheless, methane and carbon oxide can react with water to give carbon dioxide and hydrogen. The maxima of CO_2 formation appear at 330, 400 and 690°C and the maximum of hydrogen formation is at 400°C. On the other hand, in the reaction over the catalyst $Pt–Mo/Al_2O_3$ the enhanced release of CH_4, CO_2 and H_2 is observed. Carbon dioxide is liberated already starting from 130°C, but the maxima of its formation occur at 290, 390 and 700°C, while the maxima of hydrogen formation are at 400 and 680°C.

Conclusions

Analysis of the intensity and positions of peaks on the TPR profiles shows that depending on the composition of the catalysts and conditions of the thermal treatment (temperature of oxidation and temperature of TPR–H_2) different surface groups are formed in different amounts on the surfaces of Mo/Al_2O_3 and $Pt–Mo/Al_2O_3$. A change in the reducing agent from H_2 to CO results in significant changes in the systems studied. Hydrogen interacts mainly with molybdenum or platinum-molybdenum groups causing a decrease in the degree of oxidation of these metals, while carbon oxide stimulates multidirectional chemical reactions.

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