

THERMAL CHARACTERISATION OF ALUMINA SUPPORTED CHROMIUM AND PLATINUM–CHROMIUM CATALYSTS

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This study presented results on reduction of alumina supported chromium and platinum–chromium catalysts using temperature programmed reduction method (TPR). It has been shown that catalysts after earlier oxidation step but without calcinations one undergo reduction in lower temperature in comparison to calcined only catalysts. Moreover, addition platinum to Cr/Al₂O₃ catalysts also caused decrease of reduction temperature. It has been observed that over the examined catalysts oxidation CO to CO₂ and reduction CO to CH₄ occurs. However, on Pt–Cr catalysts both reactions proceed at lower temperature compare to Cr catalysts.

Keywords: Cr/Al₂O₃, Pt–Cr/Al₂O₃ catalysts, TPR–H₂, TPR–CO

Introduction

Catalysts containing platinum and chromium species supported on alumina and other solids, prepared in various ways, have been studied by several groups [1–3]. These catalysts become increasingly interesting to many authors in last years. Bimetallic system have been demonstrated to modify the catalysis of each component and create new catalytic properties. As was reported [4] Pt–Cr bimetallic catalysts show higher activities than Pt or Cr monometallic catalysts.

Our earlier study on the characterisation and structure of the catalysts Pt–Cr/Al₂O₃ [5] has proved their high catalytic activity in the reaction of methane oxidation [6]. A recent study [7] has shown their high catalytic activity in the reaction of simultaneous elimination of organic compounds of sulphur and nitrogen by hydrogenolysis of the bonds C–S and C–N. This paper reports results of the study of these catalysts by the temperature programmed reduction described earlier [8].

Experimental

The catalysts were prepared by the method of incipient wetness using the solution of chromium nitrate, while platinum was deposited using a solution of hexachloroplatinic acid according to a procedure described earlier [5].

Prior to the TPR measurements with the use of hydrogen or carbon monoxide, the catalysts samples were subjected to calcination and oxidation or only ox-

idation. The TPR measurements were carrier out on the apparatus AMI I, with a katharometer as a detector for the samples reduced by hydrogen (5% H₂/95% Ar) or a quadrupole mass spectrometer made by Dycor for the samples reduced with CO (5% CO/95% Ar). Two series of measurements were performed – one for the samples subjected to calcination at 500°C for 5 hours and oxidation in the atmosphere of O₂ (5% O₂/95% Ar) and the other one for the samples subjected to oxidation only. In the first series of measurements the TPR curves were recorded for the samples of about 100 mg at the gas flow rate of 50 cm³ min⁻¹, the temperature increase rate of 20°C min⁻¹ and the time of heating of 30 min. The samples were oxidized at 400 (curve 1), 500 (curve 2) and 700°C (curve 3) and then they were subjected to the temperature programmed reduction with hydrogen (TPR–H₂).

In the third series of measurements, the samples were subjected to oxidation at 500°C then temperature programmed reduction with carbon monoxide (TPR–CO) at 700°C, at the gas flow rate 40 cm³ min⁻¹ and the temperature growth rate of 15°C min⁻¹. During oxidation the sample of 200 mg having been heated to a desired temperature, was annealed at that temperature for 30 min, while during the TPR–CO measurements it was done for 10 min.

Results and discussion

The TPR measurements were performed for the preparations listed 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 ₂ O ₃ (Degussa)	93
0.3 [#] Pt/Al ₂ O ₃	93
2Cr/Al ₂ O ₃	92
20Cr/Al ₂ O ₃	76
0.3Pt-2Cr/Al ₂ O ₃	95
0.3Pt-20Cr/Al ₂ O ₃	77

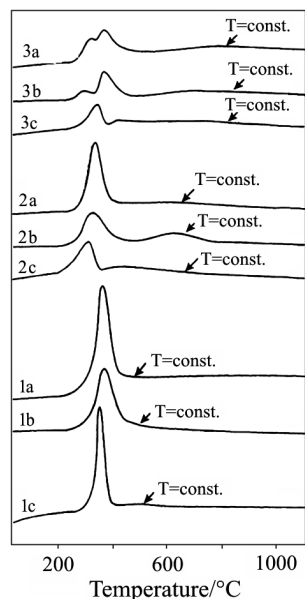
**Fig. 1** TPR-H₂ profiles for a, b – 2Cr/Al₂O₃ and c – 0.3Pt-2Cr/Al₂O₃ samples calcined at 1 – 400°C, 2 – 500°C and 3 – 700°C

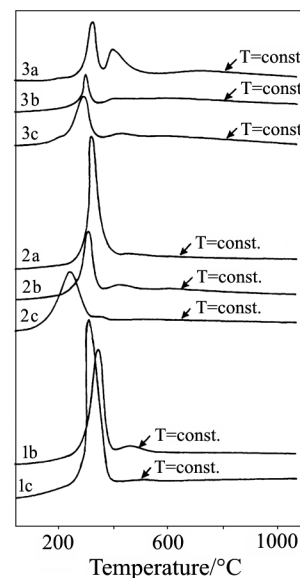
Figure 1 presents the TPR-H₂ profiles for the samples of 2Cr/Al₂O₃ calcined at 500°C subsequently subjected to oxidation at 400, 500 and 700°C (curves 1a, 2a, 3a) and for the same preparations but subjected to oxidation without a preliminary calcination (curves 1b, 2b, 3b). A comparison of the TPR-H₂ profiles reveals that the peaks obtained for the samples subjected to calcination followed by oxidation at 400 and 500°C (curves 1a and 2a) are much greater than the corresponding ones recorded for the samples oxidised without preliminary calcination (curves 1b and 2b). When oxidation was performed at 700°C, the TPR profiles obtained for the calcined and oxidised sample and the only oxidised one are similar with the maxima at the same temperatures (curves 3a and 3b). The maxima in the TPR-H₂ profiles obtained for the samples of 0.3Pt-2Cr/Al₂O₃ subjected to oxidation occur at temperatures higher than the maxima obtained for 2Cr/Al₂O₃ (curves 1c, 2c), when the samples are reduced at 400 and 500°C. The TPR-H₂ profile for the

samples with platinum recorded at 700°C (curve 3c) shows only one peak, while an analogous profile oxidised for 2Cr/Al₂O₃ shows two maxima. The maximum in the TPR profile of the sample 0.3Pt-2Cr/Al₂O₃ occurs at a temperature intermediate between those of the two peaks recorded for 2Cr/Al₂O₃.

Figure 2 presents the TPR-H₂ profiles of the samples 20Cr/Al₂O₃ and 0.3Pt-2Cr/Al₂O₃. The profile obtained for the sample of 20Cr/Al₂O₃ showed peaks at much lower temperatures than those of the peaks recorded for the samples with 2 mass% Cr, which means that reduction of the samples with 20 mass% Cr is easier. In all samples presented in Fig. 2 the consumption of hydrogen was elevated, which is obvious taking into account a higher content of chromium. Preliminary calcination of the samples of 20Cr/Al₂O₃ (curves 2a, 3a) results in much greater consumption of hydrogen than when the samples are subjected to oxidation only (curves 2b and 3b). For the samples 0.3Pt-2Cr/Al₂O₃ an increased consumption of hydrogen was observed at lower temperatures than for the preparations without platinum.

The TPR-H₂ profiles slightly higher temperature than for the samples Cr/Al₂O₃ subjected to oxidation only obtained revealed peaks with maxima at different temperatures. In general, the consumption of hydrogen during TPR measurements for the samples Cr/Al₂O₃ preliminary calcined and then oxidised was higher and occurred at a slightly higher temperature than for samples Cr/Al₂O₃.

The Cr/Al₂O₃ samples subjected to calcination at 700°C and oxidation and then reduction with hydrogen contain two types of reduced species. According

**Fig. 2** TPR-H₂ profiles for a, b – 20Cr/Al₂O₃ and c – 0.3Pt-20Cr/Al₂O₃ samples calcined at 1 – 400°C, 2 – 500°C and 3 – 700°C

to our earlier study [9] the samples Cr/SiO₂ calcined in high temperatures were found to contain Cr²⁺ ions in at least two different coordinatively unsaturated forms. The type of Cr ions corresponding to the maximum at a higher temperature does not occur in the preparation 20Cr/Al₂O₃ subjected to oxidation only but it is present in the oxidised 2Cr/Al₂O₃. The increase in the content of chromium in the preparations Cr/Al₂O₃ results in a significant decrease in the reduction temperature. For the catalysts containing 0.3 mass% platinum the maxima of hydrogen consumption were observed at temperatures lower than for the catalysts without platinum. Moreover, it was found that the catalysts Pt–Cr/Al₂O₃ oxidised in lower temperatures used greater amounts of hydrogen in the process of reduction.

The samples of 2Cr/Al₂O₃ and 0.3Pt–2Cr/Al₂O₃ preliminary oxidised at 500°C, were also subjected to TPR with carbon oxide, the profiles obtained are shown in Fig. 3. The products of this reduction contained CO and CH₄.

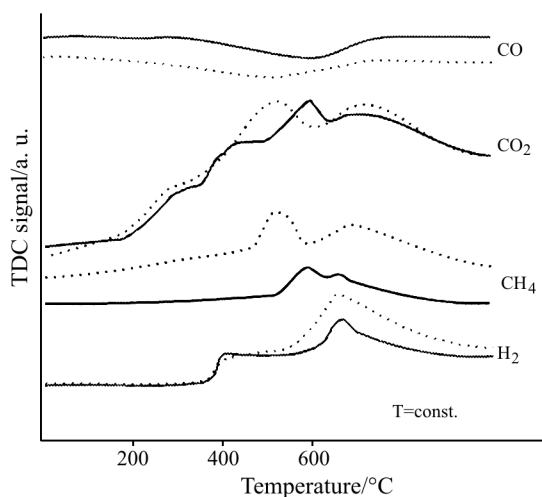


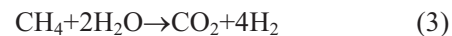
Fig. 3 TPR–CO profiles for ... – 2Cr/Al₂O₃ and — — 0.3Pt–2Cr/Al₂O₃ samples

The presence of these compounds means that apart from the use of CO for the reduction of Pt and Cr groups, it is also used for formation of CH₄ and oxidation to CO₂. The latter process starts already at about 200°C, whereas the reduction of CO to CH₄ requires temperatures of about 500°C.

As follows from the curve characterising the formation of CO₂, the catalysts studied must have at least four different types of surface groups responsible for the oxidation but for formation of CH₄, according to the reaction:



two different surface groups take part in reduction. The water formed during the reaction can be involved in the following reactions:



The observed decrease in CO consumption in the range 400–600°C confirms the occurrence of reactions (1) and (2).

Introduction of a small amount of platinum into the preparation 2Cr/Al₂O₃ results in a decrease in the temperatures of formation of CO₂ and CH₄. As follows from the above results, the catalyst 0.3Pt–2Cr/Al₂O₃ can actively catalyse the process of formation of CH₄ from CO, and H₂ and CH₄ oxidation to CO₂. This latter conclusion has been already indicated in our earlier study [6].

Conclusions

As follows from the above discussed results, for the catalysts subjected to oxidation without the stage of calcinations, the reduction process occurs at lower temperatures. It has been shown that an addition of platinum to Cr/Al₂O₃ catalysts leads to a decrease in the reduction temperature.

On the surface of the catalysts studied carbon monoxide undergoes oxidation to CO₂ and reduction to CH₄. An addition of platinum to the catalysts results in a decrease in the temperature of the reactions leading to formation of these products.

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