Synthesis of CrO_x/Al_2O_3 catalyst in sol-gel conditions[*]

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A series of CrO_x/Al_2O_3 samples with various Cr/Al molar ratios (0.1-1.0) have been synthesized by the sol-gel technique from $Al(C_3H_7O)_3$ (aluminium isopropoxide) and chromic acid precursors. The synthesis applied allowed obtaining the final product in monolithic (nonfractured upon drying) form with no use of drying control chemical additives. All samples are characterized by thermal analysis, XRD, and TEM. The low temperature nitrogen adsorption measurements indicate the presence of mesopores. The use of the sol-gel technique permitted a high degree of homogeneity of binary systems up to the Cr/Al molar ratio of 0.5.

1. INTRODUCTION

The activity of CrO_x/Al_2O_3 catalysts (particularly in dehydrogenation reactions) has been studied for a few decades and presently the catalysts are used on a commercial scale (the Houdry® process) to produce propene and -butene from the corresponding paraffins [1-3]. These olefins are used for production of various important commodity chemicals such as polypropylene, propylene oxide, and isooctene. It should be stressed that supported chromium oxide-based catalysts have also found industrial application in polymerization of ethylene [4,5], oxidation of alcohols [6-8], selective oxidation of cyclohexane [9] and in catalytic reduction of NO_x to NH_3 [10-12]. Moreover, catalysts of this type can

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[*]This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th birthday

be applied in oxidative dehydrogenation of isobutane to isobutene [13,14], which is a substrate in production of MTBE and methacrylate.

Chromium can occur at the oxidation states 6+, 5+, 3+ and 2+, depending on the applied pretreatment, Cr concentration and the type of support. For the of catalysts with low loading, chromium is anchored on Al$_2$O$_3$ support mainly as Cr^{6+} , whereas for highly loaded ones the catalysts also contain Cr^{3+}, which resists oxidation [1,15-16]. It is generally accepted, that Al$_2$O$_3$ support appears to stabilize Cr^{3+} against reduction below the 3+ state under dehydrogenation conditions [17]. According to A. Hakuli [1], Cr^{3+} sites are active in dehydrogenation. Usually, CrO$_x$/Al$_2$O$_3$ catalysts are prepared from Cr(NO$_3$)$_3$ or CrO$_3$ solution by impregnation. In the present study, we applied sol-gel method for preparation of CrO$_x$/Al$_2$O$_3$ catalysts. The aim of the study was to develop and test a new method for the obtaining of CrO$_x$/Al$_2$O$_3$ catalyst that would permit introduction of chromium at the oxidation state 6+ in order to use the coordination properties of chromium atoms for making a stable and developed gel network with aluminium oxide. On the basis of our earlier works in which we succeeded in obtaining a wide gamut of binary oxide systems by the sol-gel method, the matrix dispersing the precursor of chromium oxide was aluminium gel obtained by hydrolysis of aluminium isopropylene. In our earlier studies into a gel matrix of Al$_2$O$_3$ we introduced the oxides at the oxidation degree 2+, MgO [18], 3+, B$_2$O$_3$ [19] and 4+ SnO$_2$ and GeO$_2$ [20-23]. When chromic acid was used, a stronger effect of co-gelation of the components was expected because of the properties of Cr^{6+} ions.

2. MATERIAL AND METHODS

2.1. Synthesis

A 20% water solution of chromium anhydride CrO$_3$ in the amount corresponding to the target molar ratio was added to alumina gel synthesised by the method described in our earlier work [18], see Table 1. The gels obtained were characterised with a high degree of cross-section manifested in a considerable increase in viscosity, proportional to the amount of chromium component introduced. The gel obtained was placed under vacuum to evaporate into a powder. The powder was characterised by the methods given below.

The X-ray powder diffraction patterns of the samples were taken on Philips PW1050 diffractometer, with Ni filtered CuKα radiation. Reflection positions, half bandwidth as well as intensity were calculated by the APD Philips program. Before the XRD investigation the samples were heated at 773K in air atmosphere for 6 hours. Additional diffractograms were recorded of the samples calcined in air after washing with water.

Tab. 1. Composition of the materials obtained.

System	CrO_x/Al_2O_3 0.1	Al_2O_3/CrO_x 0.5	Al_2O_3/CrO_x 1.0
Molar ratio Cr:Al	10:1	5:1	1:1
Sample	Cr/Al 0.1	Cr/Al 0.5	Cr/Al 1.0

The surface morphology of the oxides was depicted by scanning electron microscopy (*Philips*) and the structure was characterized by transmission electron microscopy (JEOL 200 CX *Jeol*).

The porous structure was determined by the low temperature (77K) nitrogen adsorption measurements carried out at on an Accelerated Surface Area and Porosimetry System model 2010 V2.00 D made by Micrometrics, using 200-300 mg of calcined materials of the grain size fraction between 0.1-0.2 mm. Prior to nitrogen adsorption all samples were outgassed at 623K at 0.4 Pa till constant weight. Both adsorptive and desorptive branches of the isotherm were taken in the range of p/p_0 0-1.

2.2. Thermal analysis

Thermal transformation of the gel samples was carried out on a SETSYS 12 (Setaram – France) in the same conditions. A 20 mg sample was placed in alumina crucible (volume –100 mm^3) and heated at a rate of 5K min^{-1} up to 1273K. For all experiments we used the grain size fraction between 0.05 and 0.1 mm. The above fraction has been set apart from the powder obtained by grinding in an agate mortar. The TA-TG traces were recorded in air atmosphere. For thermal analysis we used air-dried samples.

2.3. Temperature programmed reduction

Temperature programmed reduction (TPR) analysis was made in an apparatus made by Micrometrics Pulse ChemiSorb 2705 with a TDC detector on the samples of 50 mg and grain size fraction below 0.1mm. Prior to measurement, the samples were activated at 673K under helium flow at the rate of 25cm^3/min for 1 hour. After cooling the sample and the furnace to room temperature, measurements were made in the range from 293K to 1373K, at the temperature gradient of 10° /min. The reduction mixture containing 10% v/v of hydrogen in argon was blown through the reaction system at the rate 40cm^3/min. The steam formed as a result of reaction of hydrogen with the oxide was frozen with the use

of a mixture of isopropanol and liquid nitrogen prior to the stage of detection by TCD. The TPR analysis was made for all systems studied that had been earlier subjected to calcination for 6 hours at 773K in an oxidising atmosphere.

3. RESULTS AND DISCUSSION

Nitrogen adsorption isotherms were determined for the composite oxide materials and pure Al$_2$O$_3$ $_{gel}$ after calcination at 773 K. Figure 1 presents a comparison of distributions of pore volume in pure Al$_2$O$_{3-gel}$ and binary oxide system. The isotherm shape is IVa type, where, generally, the location of the adsorption branch of the isotherm is governed by delayed condensation. The loop related to the capillary condensation in mesopores is relatively narrow and the adsorption and desorption branches being almost vertical and nearly parallel, which suggests a loop type H2. Taking into consideration general recommendation in relation to validity of the derived pore size distribution for type IVa isotherm, the desorption branch was adopted for standard BJH method. As follows from the data obtained (Figure 1) the chromium component introduced into the binary oxide system leads to a decrease in the pore diameters with respect to those occurring in Al$_2$O$_{3-gel}$. The diameters of pores contributing to the cumulative pore volume (Table 2) are by about 1.5 nm smaller than those in pure alumina gel. The exception was the sample CrO$_x$/Al$_2$O$_3$ -1.0 for which a large variety of pore diameters was found. This observation seems to be related to the high inhomogeneity of the sample as the TEM images show that chromium oxide was not fully built into the alumina gel structure. Moreover, for lower contents of chromium precursor the chromium component acts as a textural promoter increasing the specific surface area of the system (Table 2) because of a reduced pore diameters.

Tab. 2. Texture parameters calculated from N$_2$ isotherms.

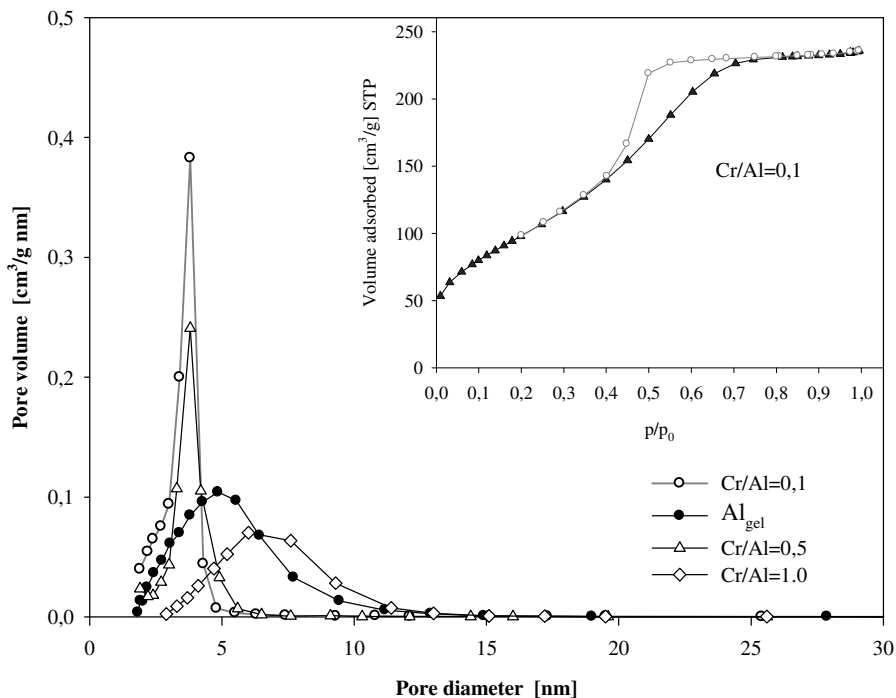| Sample	Cumulative Pore Volume [cm^{3}g^{-1}]	Average Pore Diameter [nm]	S$_{BET}$ [m^{2}g^{-1}]
Al$_2$O$_3$ $_{gel}$	0.48	4,9	298.2
Cr/Al 0.1	0.39	3.39	363.0
Cr/Al 0.5	0.28	3.71	304.2
Cr/Al 1.0	0.37	6.69	169.0

Fig. 1. A comparison of pore volume distributions for the binary gel samples with different molar ratios of Cr:Al. For comparison the curve for Al_2O_3 gel is included.

According to X-ray diffraction analysis, the systems obtained are to a considerable degree amorphous. The diffractograms of Cr/Al 0.1 and Cr/Al 0.5 (Figure 2a,b) show no reflexes attributable to CrO_3 phase, but broad reflexes assigned to γ-Al_2O_3 phase. Thus, it is reasonable to suppose that in these samples chromium(VI) oxide did not form larger agglomerates or crystallites, but most probably it exists in layers or has been built into the gel network. Only for the sample of the highest content of chromium(VI) oxide the diffractograms show well-developed reflexes attributable to the CrO_3 phase (Figure 5). After washing with water, the reflexes assigned to CrO_3 disappeared as a result of dissolution and washing out of this compound. This observation suggests that for so high content of CrO_3 in the system, some part of it has not been permanently built into the gel network and has been left outside the network forming crystals.
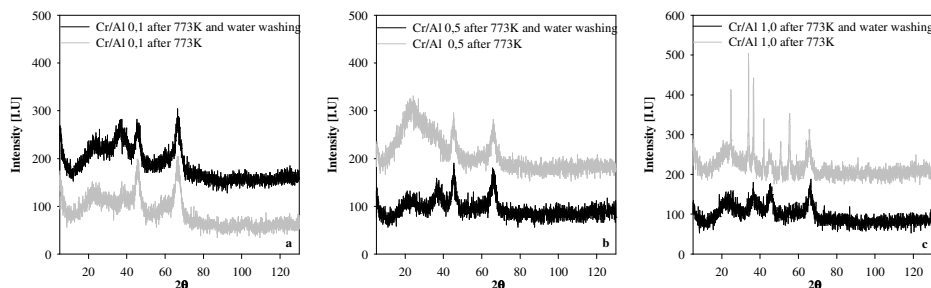
Fig. 2. XRD patterns for binary gel samples with various Cr/Al ratio.

This supposition is confirmed by TEM images. Figure 3 presents the TEM photograph taken of Cr/Al. 1.0 sample not washed with water and shows the presence of crystalline forms, most probably of chromium(VI) oxide. The results are in agreement with literature data according to which the CrO$_x$/Al$_2$O$_3$ system contains chromium mainly as Cr^{3+} and Cr^{6+}, and in trace amounts as Cr^{5+} [24,26].
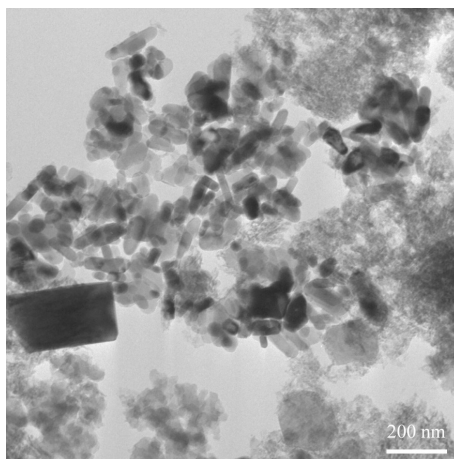

Fig. 3. TEM pictures for Cr/Al 1,0.

The TPR profiles of the systems synthesised bring information on the quantitative contribution of Cr^{6+}, which undergoes reduction to Cr^{3+} in reaction with hydrogen. Reduction of all samples takes place in a similar temperature range (Figure 3, Table 3), but the systems containing the greatest total amount of chromium undergo reduction at a lower temperature.
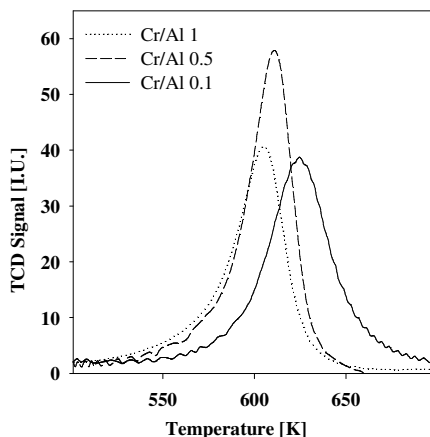
Fig. 4. TPR curves for binary oxides samples.

Tab. 3. Maxima of TPR profiles.

Sample	Cr/Al 0,1	Cr/Al 0,5	Cr/Al 1
T max [K]	624	611	605

These results confirm that in the conditions of dehydrogenation, chromium at higher degree of oxidation is reduced to Cr^{3+}, which is active in reactions with hydrogen [1, 24-26]. An interesting observation is that the amount of hydrogen used for reduction of all samples studied was similar. It suggests that for the systems with higher content of chromium oxide, chromium is reduced already at the stage of preparation as a result of Cr^{6+} reaction with alcohol. There is no doubt that at the stage of preparation the alcohol present in the reaction environment undergoes oxidation as the gel densified on the evaporator was observed to get darker and the condensation products obtained after gel drying were found to contain aldehydes. Interpretation of TPR results in view of those of the earlier X-ray diffraction study indicates that when high amount of Cr^{6+} is introduced to the systems studied it is not built into the alumina gel structure and that is why its reduction is possible.
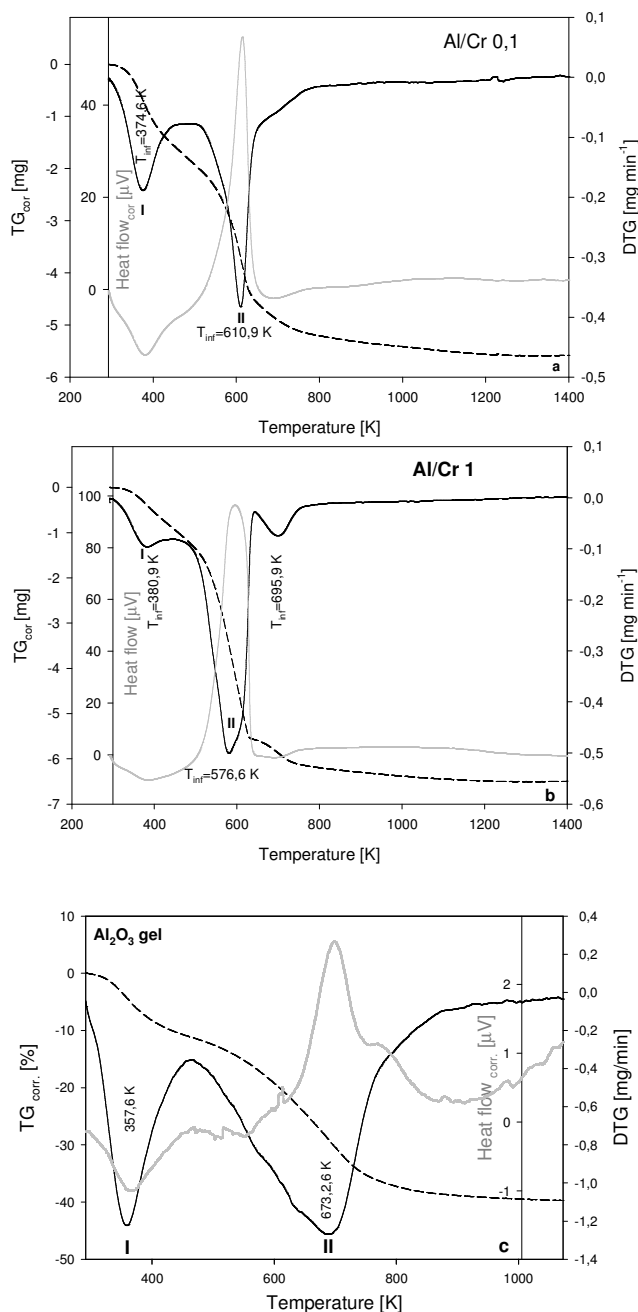
Fig. 5. TG-TA-DTG curves for binary oxides air-dried samples (a,b). For comparison the air-dried alumina gel sample is included (c).

The thermogravimetric results indicate great similarity between the samples studied in this work and the earlier studied binary gel systems. Similarly as concluded in our earlier works, the alumina matrix seems to determine the character of the binary oxide material. The character of TG/TA curves is similar as for pure alumina gel. Maximum (I) on TG curve is interpreted as related to elimination of water and corresponds to the endothermic peak on TA curve, while maximum (II) on TG curve is related to combustion of organic residues in air atmosphere and is also reflected on TA curve. It should be noted that for the systems containing chromium component, maximum (I) on TG curve is shifted towards higher temperatures (~20K) which can indicate stronger cross-linking of these samples than that of alumina gel. Another characteristic feature of binary oxide gels CrO_x/Al_2O_3 is that the exothermic peak corresponding to the oxidation of organic residues is shifted towards lower temperatures and the oxidation process takes place in a narrower range of temperatures. This shift for the binary oxide systems is considerable relative to that observed for the analogous oxidation process in alumina gel and its magnitude increases with increasing content of the chromium component. For the sample with the highest content of chromium component (Cr/Al 1) this maximum is shifted by almost 100K.

4. CONCLUSIONS

A new method for the obtaining of binary oxide systems CrO_x/Al_2O_3 based on the sol-gel processes is presented. The use of a precursor of the second oxide component (CrO_3) with Cr 6+ permitted very strong gelation so also very strong cross-linking of the system obtained. Thanks to this strong cross-linking it was possible to observe the chromium component to be permanently built into the structure of alumina gel. The exception was the system of the highest content of chromium for which crystallisation of the excess amount of chromium oxide was noted.

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