

Investigation of the chromium oxide system by means of temperature-programmed reduction

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Abstract

A temperature-programmed reduction study of Cr_2O_3 samples prepared at 673 and 1073 K in different gaseous media, air or helium, was carried out. It was established that one or two peaks arise from the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition for samples treated in air or inert gas, respectively. Results of chemical analysis, X-ray diffraction and adsorption measurements suggest that the different behaviour of the samples as evident from TPR is due to differences in the structural and adsorption features, namely variable degrees of crystallization, crystal defects and different access to the surface. An explanation of the mechanism of reduction is proposed.

Keywords: Chromium oxide; Reduction mechanism; Structure; Temperature-programmed reduction

1. Introduction

It is known that the phase change in chromia, from amorphous to α -form, occurs at 673 K and is promoted by the presence of gaseous oxygen [1–3]. However, under inert atmosphere or vacuum, this transfer requires temperatures over 723 K [4]. Structural studies of the metal oxide, prepared by calcination at 673 K in air or inert gas, are of interest because the presence of either the crystalline or amorphous form of the metal oxide is essential for its catalytic activity in certain reactions, e.g. selective NO reduction by ammonia in the presence of oxygen [5], methylcyclopropane isomerization and hydrogenolysis [6].

In the present work, an attempt is made to correlate the specific features of experimentally obtained temperature-programmed reduction (TPR) spectra of Cr_2O_3 samples, treated at various temperatures and in different gaseous media, to differences

in the structure of these samples. Such investigations are of importance for the scientific basis of the preparation and selection of chromia-based catalysts.

2. Experimental

Chromium hydroxide samples were prepared from $\text{Cr}(\text{NO}_3)_3$ by precipitation with ammonia at 303 K and $\text{pH} = 6.0$ in a Contalab automatic laboratory reactor (Con-traves, Switzerland). After washing, the precipitate was calcined at 673 K for 4 h in air or in helium flow, denoted as Cr_2O_3 (673 air) and Cr_2O_3 (673 He), respectively. A Cr_2O_3 (1073 air) sample was prepared by heating a Cr_2O_3 (673 air) sample to 1073 K in a flow of air at a rate of 15 K min^{-1} and kept at the same temperature for 10 min. The same procedure was used to prepare a Cr_2O_3 (1073 He) sample from Cr_2O_3 (673 He) in helium flow. The specific surface area of the samples was measured by the BET method. Differential thermal analysis (DTA) indicated no traces of undecomposed nitrates after calcination, which means that the TPR profiles were due exclusively to hydrogen consumption. All the TPR measurements were carried out by means of an apparatus described elsewhere [7]. A cold trap, 233 K, for removing water during reduction was mounted in the gas line ahead of the thermal conductivity detector. A hydrogen–argon mixture (10% H_2), passed over a molecular sieve at 233 K, was used to reduce the samples at a flow rate of 24 ml min^{-1} . The temperature was linearly raised at a rate of 15 K min^{-1} . In some cases, an argon–hydrogen mixture (21% H_2) was applied. The detector was calibrated on the basis of TPR data on H_2 consumption with various amounts of stoichiometric NiO calcined at 1073 K under the conditions described above. A quartz reactor loaded with 0.03 g of material was utilized for the experiments with chromia samples. The amount of loaded sample was determined through the equation proposed by Monti and Baiker [8]

$$k = \frac{S_0}{V^* c_0} \quad (1)$$

where k is a characteristic number (s), S_0 is the amount of reducible species (μmol), V^* is the total flow rate of the stream ($\text{cm}^3 \text{ s}^{-1}$), and c_0 is the initial hydrogen concentration ($\mu\text{mol cm}^{-3}$).

According to these authors [8], the recommended range for k is between 55 and 140 s for heating rates from 6 to 18 K min^{-1} . In this study we accepted $k = 100 \text{ s}$.

The content of surface Cr^{+6} ions was chemically determined by means of repeated water extraction of the samples. The presence of bulk Cr^{+6} ions in some of the samples was determined by the Bunsen–Rupp method [9], the amount of Cr^{+6} ions (wt%) being related to the soluble part of Cr_2O_3 in this case.

The chromia surface reduction activity was checked by the interaction with I_2 (hexane) in the absence of moisture and oxygen according to the method described in Ref. [10].

X-ray powder diffraction measurements were performed using $\text{Cu K}\alpha$ radiation and scintillation registration. The average crystallite sizes were estimated from the Fourier transformed (104) and (110) diffraction lines corrected according to the method of Stokes. This method is described in detail in Ref. [11].

Transmission electron microscopy (TEM) micrographs were taken on a JEM 100 M microscope.

Pore size distributions of Cr_2O_3 (673 air) and Cr_2O_3 (1073 He) were determined by the method of Pierce [12].

3. Results and discussion

Fig. 1 shows TPR spectra of the chromia samples. Together with Cr^{+3} , Cr^{+6} ions may be present as chemical defects. Although stable on supported chromia, we did not consider the occurrence of Cr^{+5} ions, since they are not stable on unsupported Cr_2O_3 [13]. For thermodynamic reasons, the reduction of bulk chromia, taking place in the surface layers, does not yield Cr^+ and Cr^0 . The standard free energy change ΔG^0 for Cr_2O_3 at the temperature of reduction has a high positive value (100 kJ mol^{-1}) and because of this the reduction process proceeds as a consequence of water vapour removal from the reaction zone. In this case, the expression $RT \log(P_{\text{H}_2\text{O}}/P_{\text{H}_2})$ from the equation [14]

$$\Delta G = \Delta G^0 + RT \log(P_{\text{H}_2\text{O}}/P_{\text{H}_2}) \quad (2)$$

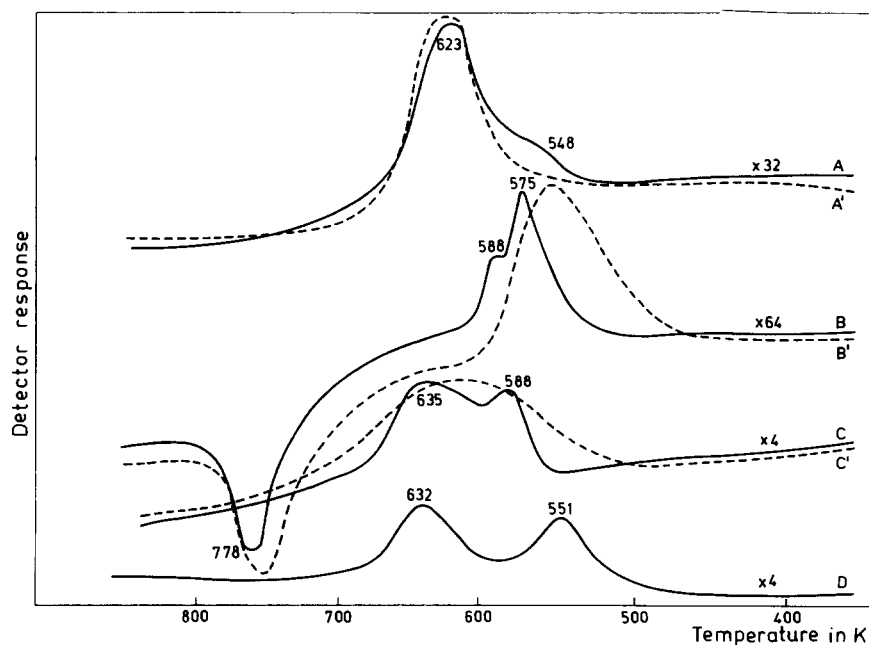


Fig. 1. TPR spectra of chromia samples: A, Cr_2O_3 (673 air); A', Cr_2O_3 (673 air) after water extraction; B, Cr_2O_3 (673 He); B', Cr_2O_3 (673 He), 21% H_2 in the reducing mixture; C, Cr_2O_3 (1073 He); C', Cr_2O_3 (1073 He), 21% H_2 in the reducing mixture; D, Cr_2O_3 (1073 air).

is sufficiently negative. Therefore, the observed peaks are due to the transitions $\text{Cr}^{+6} \rightarrow \text{Cr}^{+3}$ and/or $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$.

Table 1 presents a summary of the results of the chemical analysis, and X-ray diffraction and adsorption measurements. The results indicate that the chemical and structural features of the samples are directly dependent on the preparation conditions.

Along with a peak with $T_{\text{max}} = 623$ K due to the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition, a shoulder at about 548 K is also observed in the TPR spectrum of Cr_2O_3 (673 air) (Fig. 1, curve A). This shoulder is associated with the presence of Cr^{+6} in that sample. No shoulder was detected after water extraction (Fig. 1, curve A').

The TPR profile of Cr_2O_3 (673 He) exhibits peaks with T_{max} at 575 and 588 K. The former peak cannot originate from Cr^{+6} ions because chemical analysis showed that their content was negligible. A question arises as to why two TPR peaks should be responsible for the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition. Similar TPR patterns have already been published but so far no explanation has been proposed [5]. First, we assumed that the presence of two TPR peaks might be due to a low degree of crystallization, i.e. the occurrence of both an amorphous phase and a crystalline phase, the former being readily reducible. According to chemical analysis, the Cr_2O_3 (1073 He) sample does not contain Cr^{+6} ions (Table 1) but the TPR spectrum also demonstrates two peaks with T_{max} at 588 and 635 K, the area of the former peak being decreased with respect to that of the latter peak. This coincides with our suggestion that the amorphous phase is reduced first followed by reduction of the crystalline phase. However, X-ray diffraction data are in disagreement with this assumption because the Cr_2O_3 (673 He) sample is completely amorphous whereas Cr_2O_3 (1073 He) is a well-crystallized sample. Therefore, this interesting experimental result of two TPR peaks due to the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition, needs another explanation.

The next assumption which we made was that the peak splitting might be due to incorrect experimental operating variables since the calculations according to the equation of Monti and Baiker were performed with an S_0 value for the total amount of

Table 1.
Summarized results of the chemical analysis, X-ray diffraction and adsorption measurements

Sample	Cr^{+6} content (wt. %)	Redox strength (mmol $\text{I}_2 \text{g}^{-1}$)	D (Å)	H (Å)	S_{XRD} ($\text{m}^2 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	L_{BET} (Å)
Cr_2O_3 (673 air)	1.2	0.051	256	184	51	55	209
Cr_2O_3 (1073 air)	29.8 ^a	–	494	390	25	25	460
Cr_2O_3 (673 He)	0.1	0.162	–	–	–	134	86
Cr_2O_3 (1073 He)	–	–	288	261	41	27	426

^a amount of Cr^{+6} ions in the dissolved part of Cr_2O_3 determined by the Bunsen-Rupp method;

D —crystallite diameter;

H —crystallite height;

S_{XRD} —surface area estimated from X-ray diffraction data;

S_{BET} —BET area;

L_{BET} —effective particle size estimated from the BET area.

loaded sample. The intrinsic amount of reducible species is lower because with this metal oxide the reduction process proceeds in the surface layers without reaching the centre of the grain. Estimations of the amount of hydrogen consumed during TPR showed that the reduced part of the sample was 6.33% for Cr_2O_3 (673 air), 6.80% for Cr_2O_3 (673 He) and 0.66% for Cr_2O_3 (1073 He). A certain inaccuracy can be expected because the amount of hydrogen consumed for the $\text{Cr}^{+6} \rightarrow \text{Cr}^{+3}$ transition in the Cr_2O_3 (673 air) sample cannot be strictly determined, whereas with the Cr_2O_3 (1073 He), the negative peak event interferes with the H_2 uptake, the intrinsic amount of consumed hydrogen thus being higher than calculated. In spite of this, these data show that the reduction process takes place in the surface layers of the metal oxide. The probability of k being less than 55 is higher for the Cr_2O_3 (1073 He) sample since it has a lower BET area ($27 \text{ m}^2 \text{ g}^{-1}$). Moreover, it can be seen from the TPR spectrum that the amount of consumed hydrogen is considerably smaller (about 10 times) as compared to Cr_2O_3 (673 air) and Cr_2O_3 (673 He). If the observed effect was related to $k < 55$, then it should be enhanced with the increase in hydrogen concentration in the reducing mixture (the increase in c_0 should yield lower values of k , Eq. (1)). However, TPR experiments with 21% hydrogen showed no peak splitting (Fig. 1, curves B' and C'). Hence, this effect cannot be associated with incorrectly selected experimental operating variables.

The TPR spectrum of Cr_2O_3 (1073 air) also manifests two peaks but the peak with $T_{\text{max}} = 551 \text{ K}$ is due to the presence of a considerably larger amount of Cr^{+6} ions in the surface layers of the sample, determined by the Bunsen–Rupp method (Table 1). It follows that samples prepared in air give rise to one TPR peak related to the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition, whereas two peaks arise for the same transition from samples treated in helium. Apparently, these experimental facts can be explained after detailed study of the structural properties of the samples.

Summarized results from the X-ray diffraction and adsorption measurements show that the structural, morphological and textural features of the samples are substantially dependent on the preparation conditions (Table 1).

Sample Cr_2O_3 (673 air) is polycrystalline chromia. The shape of its crystals can be approximated by a cylinder whose diameter (D) is larger than the height (H). The estimated surface area from X-ray diffraction (S_{XRD}) measurements of particles of this shape and size coincides with the BET area. Obviously, the thermal treatment in air facilitates a coherent coalescence between the micro-crystallites of the starting gel to form well-formed crystals of chromia, their external surface being totally accessible to the nitrogen molecules. The Cr_2O_3 (1073 air) sample is a well-crystallized chromia with perfect crystals. The BET area of that sample also coincides with the area calculated from X-ray diffraction data and, hence, these crystallites also expose an external surface accessible to the nitrogen molecules. The situation with the samples prepared in helium is somewhat different. Sample Cr_2O_3 (1073 He) is amorphous. The mean effective particle size (L_{BET}), calculated from the BET area, is 86 \AA . Crystal particles of chromia with sizes of that order should exhibit a clear diffraction pattern: this is not observed in this case. Consequently, the crystal aggregates of this sample are formed by a great number of coherently coalesced small crystallites, their internal surface being inaccessible to the nitrogen molecules. The Cr_2O_3 (1073 He) sample has a BET area which is

considerably smaller than that determined from X-ray diffraction. Apparently, thermal treatment in helium hinders the processes of recrystallization which results in the formation of a system of pores of very small sizes. In agreement with this conclusion, a study of the pore size distribution indicated that this sample is non-porous. However, the pore size distribution in the Cr_2O_3 (673 air) sample manifested a hysteresis in its pattern ($V_{0.95} = 0.16 \text{ m}^3 \text{ g}^{-1}$). This supports the conclusion that the internal surface is completely accessible to the molecules of both nitrogen and hydrogen.

Fig. 2 shows electron micrographs of the Cr_2O_3 (673 air), Cr_2O_3 (673 He) and Cr_2O_3 (1073 He) samples which support the conclusions made above. It can be inferred that the temperature and gaseous medium have a strong influence on the structure of the prepared samples. Their different behaviour during TPR can be related to their surface areas being varyingly accessible to the hydrogen molecules.

The TPR results are interpreted in terms of the nucleation model or the contracting sphere model. The process of reduction begins according to the nucleation mechanism. The reaction interface between the nuclei of the product and the solid substrate begins to increase by two processes: the growth of the nuclei already formed, and the appearance of a new ones. At a certain stage of the reaction, the nuclei of the product have grown to such an extent that they begin to make contact with each other. From this moment the reaction interface starts to decrease because of the overlapping of the product nuclei and the total coverage of the substrate grain with a thin layer of the product. After the nucleation process has finished, the process of reduction proceeds according to the contracting sphere mechanism, its rate being controlled by either chemical or transport phenomena. Chemical control can be accomplished by diffusion from the gas stream to the particle or diffusion through the metal layer, which may or may not be porous [14,15]. Because chromia is known to readily activate hydrogen (it is used as a hydrogenation catalyst [15]), the nucleation process is expected to be fast.

Evidently, the surface of well-crystallized samples, prepared by decomposition in air, is readily accessible to hydrogen. After completing the nucleation process, the change in the mechanism of reduction does not cause the appearance of two peaks because of lack of transport limitations. In the case of samples treated in helium, the reduction first takes place according to the nucleation mechanism and the low temperature peak is attributed to this process (Fig. 1, curves B and C), which proceeds on contact of the hydrogen with only the accessible external surface. However, the consumption of hydrogen is several times lower with the Cr_2O_3 (1073 He) sample, which, having a low BET area, is practically non-porous. On completion of the nucleation process, the mechanism is changed to that of a contracting sphere, the access of hydrogen to the surface becoming strongly hindered. The appearance of a second peak can be related to reduction at the interface $\text{Cr}^{+2}\text{-Cr}^{+3}$ layer, during which the layer being reduced is moving to the interior part of the grain. This process is considerably slower which is why the second peak is shifted to higher temperatures. The difference in the peak area ratios between the low-temperature and high-temperature peaks with the Cr_2O_3 (673 He) and Cr_2O_3 (1073 He) samples is due to differences in the accessible area.

Two peaks are no longer observed upon temperature-programmed reduction with increased hydrogen content (21%) in the reducing mixture (Fig. 1, curves B' and C'). It is

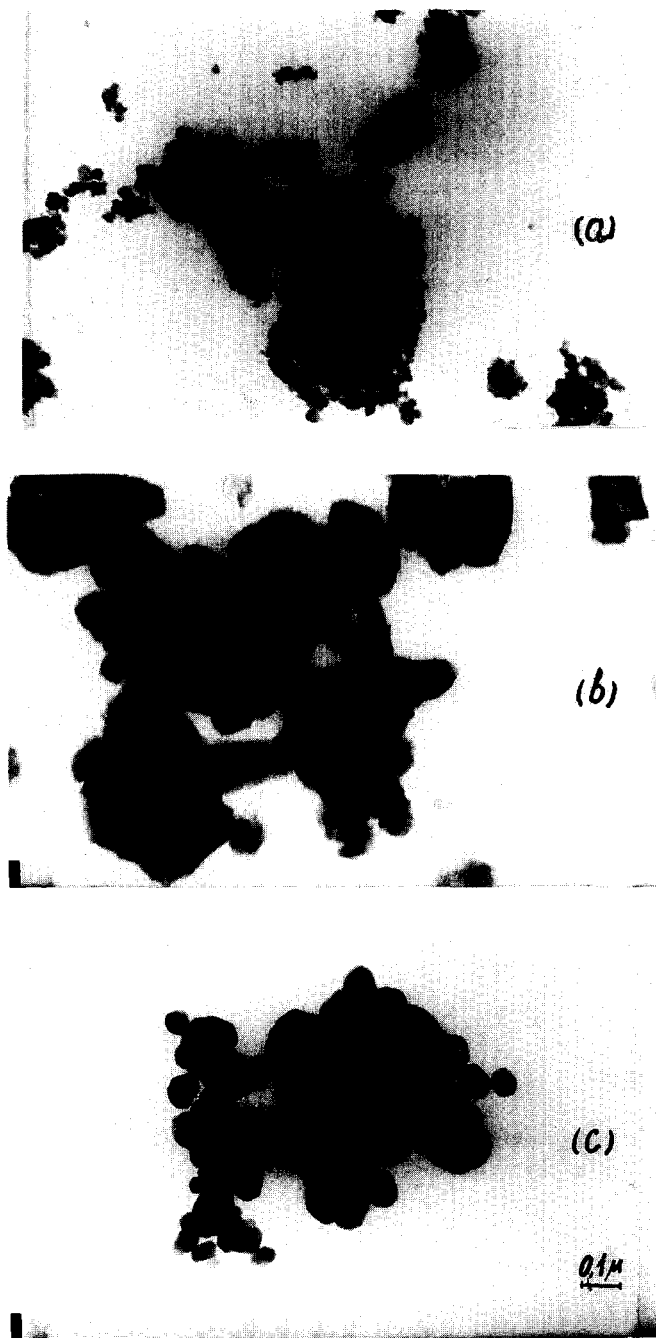


Fig. 2. TEM micrographs of chromia samples: (a) Cr₂O₃ (673 air); (b) Cr₂O₃ (673 He); (c) Cr₂O₃ (1073 He).

very probable that the higher content of hydrogen would, to a large extent, facilitate the process of moving the reduced layer to the interior of the grain.

Sample Cr_2O_3 (673 He) is also interesting because it is the only sample which gives rise to a reverse peak at 778 K. This peak was not detected if a preliminary heating up to 1073 K in helium flow was carried out. We assume that its origin is associated with the occurrence of the process $\text{e}^{-1} + \text{H}_2\text{O} \rightarrow \text{OH}^{-} + \text{H}$ which can be realized only on highly defective Cr_2O_3 prepared by calcination at 673 K under He flow. The higher number of surface defects in the oxide prepared under inert atmosphere in comparison with that prepared in air was also confirmed by means of chemical analysis through the so-called surface reduction activity (Table 1). The values determined for samples Cr_2O_3 (673 air) and Cr_2O_3 (673 He) were 0.051 and 0.162 mmol $\text{I}_2 \text{g}^{-1}$, respectively. The higher activity of Cr_2O_3 (673 He) can be attributed in this case to the presence of defects like F centres which are able to donate an electron ($\text{I}_2 \rightarrow 2\text{I}^{-}$). In addition the presence of a highly defective surface facilitates the onset of the reduction process, which is why this sample manifests the lowest temperature of the peak maximum, $T_{\text{max}} = 575 \text{ K}$ (Fig. 1, curve B), associated with the $\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$ transition. In this sense the peak position and the peak area reflect the reactivity of a given sample. The latter is directly related to the degree of defectiveness and the degree of crystallization which are strongly dependent on the preparation conditions.

4. Conclusions

The following conclusions emerge from this study.

The number of TPR peaks cannot be simply related to the number of transitions from one oxidation state to another.

Results obtained with chromia samples decomposed under an inert atmosphere are consistent with structural, morphological and textural features which determine significant differences in their reduction activity. These results can be used as a scientific basis for the preparation of chromia-based catalysts.

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References

- [1] R.L. Burwell, G.L. Haller, K.C. Taylor and J.F. Read, *Adv. Catal.*, 20 (1969) 1.
- [2] A. Zecchina, S. Coluccha, E. Guglielminotti and G. Ghiotti, *J. Phys. Chem.*, 75 (1971) 2774.
A. Zecchina, S. Coluccha, L. Cerruti and E. Borello, *J. Phys. Chem.*, 75 (1971) 2783.
- [3] P. Ratnasamy and A.J. Leonard, *J. Phys. Chem.*, 76 (1972) 1838.
- [4] M.P. McDaniel and R.L. Burwell, *J. Catal.*, 36 (1975) 394.

- [5] H.E. Curry-Hyde, H. Musch and A. Baiker, *Appl. Catal.*, 65 (1990) 211.
- [6] N.E. Cross and H.F. Leach, *J. Catal.*, 21 (1971) 239.
- [7] N.K. Kotsev and D. Shopov, *J. Catal.*, 22 (1971) 297.
- [8] D.A. M. Monti and A. Baiker, *J. Catal.*, 83 (1983) 323.
- [9] J. Deren and J. Haber, *Ceramica* 13, Krakov, 1969.
- [10] D.H. Andreeva, M.G. Kalchev and A.A. Andreev, *Coll. Czech. Chem. Commun.*, 57 (1992) 2561.
- [11] K.P. Petrov and G.M. Bliznakov, *C. R. Acad. Bulg. Sci.*, 29 (1976) 1763.
- [12] C. Pierce, *J. Phys. Chem.*, 57 (1953) 149.
- [13] F.M. Bukaneva, Yu.N. Pecharskaya, V.B. Kazanski and V.A. Dzisko, *Kinet. Katal.*, 3 (1962) 315.
- [14] W. Hurst, S. Gentry, A. Jones and B.D. McNicol, *Catal. Rev.-Sci. Eng.*, 24 (1982) 233.
- [15] J. Haber, *J. Less-Common Metals*, 54 (1977) 243.