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Studies on Chromia Zirconia Catalysts

III. Propene Hydrogenation

A. CIMINO, D. CORDISCHI, S. DE ROSSI, G. FERRARIS, D. GAZZOLI, V. INDOVINA, AND M. VALIGI

Centro di Studio SACSO CNR, c/o Dipartimento di Chimica, Università La Sapienza, 00185 Roma, Italy

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The catalytic activity of CrO_x/ZrO_2 for propene hydrogenation has been investigated in a flow apparatus at 195 K and in a circulation apparatus at 195 to 273 K. The average oxidation state of Cr, $\bar{n}$, was adjusted to the desired value by controlled redox treatments. After heating in O_2 at 773 K ($\bar{n}$ = 5.5), the samples were progressively reduced with CO or H_2 up to $\bar{n}$ = 2.5 and subsequently reoxidized by the stepwise addition of O_2 at room temperature. In the various steps of the redox treatments, the activity for propene was tested and the ESR spectra were recorded before and after catalysis. The activity sharply increased when $\bar{n}$ was decreased from 5.5 to about 3. In the reoxidation experiments the activity remained high, from $\bar{n}$ = 2.5 to about 4, and sharply decreased thereafter. In other experiments, the selective oxidation of Cr(II) to Cr_2O_3-like species (β-species) with H_2O up to 873 K did not affect the catalytic activity. The Cr(III) species, present at $\bar{n}$ = 2.5 in addition to Cr(II), were unaffected by reaction with H_2O and hence were tentatively identified as the active centers. The fact that at most 10% of total Cr was found to be active, taken together with the catalytic behavior, suggests that the active Cr(III) species are those formed in the early stages of the reduction from mononuclear and isolated Cr(V) ions. The comparison with other chromium-supported catalysts show that the reduced CrO_x/ZrO_2 is 3.6 to 100 times more active than CrO_x/SiO_2 and CrO_x/Al_2O_3. The discussion shows that the electronic structure of Cr alone does not guarantee a high catalytic activity. The coordinative unsaturation on the active site is an additional and essential factor. © 1991 Academic Press, Inc.

INTRODUCTION

Supported chromium samples have been much studied as catalysts for hydrogenation reactions. Classical investigations by Selwood (*1, 2*) and Burwell *et al.* (*3, 4*) have been concerned with pure Cr_2O_3, chromia/alumina and chromia/silica. The latter two systems have also been studied by other authors for the hydrogenation of propene (*5, 6*) and H_2–D_2 equilibration (*7*) on well-characterized samples (*5, 6, 8*). All these studies have focused attention on the role of the oxidation state of chromium and its coordinative unsaturation. Unsaturation requirements for H_2–D_2 and hydrogenation reactions have been discussed on general grounds for inorganic oxides by Siegel (*9*). The latter approach, however, cannot take into account the important role of the matrix which, in addition to controlling the dispersion and oxidation state of chromium, can also participate in kinetically important elementary steps, such as the heterolytic dissociation of the dihydrogen molecule at cation–anion pairs. The dispersion and oxidation state of chromium depend on interaction with the support, and hence the study of different supports can help to throw light on the role of chromium species, as well as on new potentialities due to the support itself. Zirconia has an amphoteric surface, possessing weakly acid and basic sites (*10*), and is able to maintain a suitable specific surface area at temperature up to about 1000 K (*11, 12*) if Cr is present. As mentioned in Part I (*12*), it was within this framework that a program was started in our laboratory

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aimed at preparation, characterization by XRD, XPS, redox cycles (*12*), IR (*13*), ESR (*14*) and catalytic testing of H_2–D_2 equilibration (*15*), propene hydrogenation, and propane dehydrogenation. The present paper reports the hydrogenation of propene on CrO_x/ZrO_2 samples whose average oxidation number of chromium was measured during controlled reduction. In some experiments, chromium species were monitored by ESR before and after catalysis. ESR results thus obtained were in full agreement with those reported in Part II (*14*). A CrO_x/SiO_2 sample was also investigated. A comparison of ZrO_2, SiO_2, and Al_2O_3 (*5*) permits clarification of the role of the support. It is shown that reduced chromium on ZrO_2 is very active for the hydrogenation of propene. Higher turnover frequencies per total chromium atoms are indeed detected on CrO_x/ZrO_2 as compared to CrO_x/Al_2O_3 and CrO_x/SiO_2. The discussion of catalytic data in the light of the essential knowledge of the average oxidation number and surface species of chromium (*12–14*) shows that coordinatively unsaturated Cr(III) species arising from the reduction of Cr(V) are the active sites for propene hydrogenation. Whereas a role of Cr(II) on ZrO_2 is ruled out, the conclusion does not imply that Cr(II) could not be active on other matrices, as for instance on Al_2O_3 (*5*).

EXPERIMENTAL

Catalysts

Zirconia was prepared from a hydrous zirconium oxide, obtained by hydrolysis of zirconium oxychloride, dried at 383 K, and used as such or after calcination in air at 923 K. The two materials are designated as ZrO_2(383) and ZrO_2(923), respectively. Chromium-containing catalysts were prepared by contacting the zirconia with chromium trioxide solutions of various concentrations at pH 1 and then drying at 383 K. Characterization of the system by means of chemical analysis, DTA, XRD, and XPS is reported in Part I (*12*). Identification of chromium species by ESR and IR spectroscopies are reported in Part II (*14*) and Ref. (*13*), respectively. CrO_x/ZrO_2 catalysts are designated as ZC*x*(T), where *x* is the approximate Cr content (wt%) and *T* the temperature (*T*/*K*) at which the starting ZrO_2 was heated. The capital letter B identifies the preparation (see Part I).

A silica-supported chromium catalyst was prepared by impregnation of SiO_2 (Degussa Aerosil, BET surface area 330 $m^2\ g^{-1}$) with a titrated solution of chromic acid. The main features of this sample (3.15% Cr by weight, labeled SC 3) are similar to those of samples described in Refs. (*7*, *8*), where further details on preparation and characterization are given. Table 1 lists the catalysts and some of their features.

Apparatus

The experiments were carried out in an all-glass apparatus, consisting of two sections suitable for circulation and flow catalytic experiments, respectively. The first section included a circulation loop of volume 0.15 liter equipped with a magnetically driven pump (flow rate about 0.8 liter min^{-1}), a pressure transducer (MKS Baratron, sensitivity 1 Pa), and a silica reactor containing the catalyst (0.05 to 0.5 g, powder) placed on a fritted disk. Commercial devices allowed thermoregulation to ±1 K above room temperature, while cryogenic baths were employed for experiments at lower temperatures, down to 195 K. The second section of the apparatus, to which the reactor was connected by means of a four-way valve, allowed pretreatment by various gases or catalytic experiments under flow. The latter section was equipped with pressure regulators, gas purifiers (as specified below), flow controllers and meters, and a premixing chamber placed before the reactor.

The analysis of the sampled gases was performed by a gas chromatograph (DANI 3400) connected to an integrator (Hewlett–Packard 3380 A).

Procedure

Catalyst pretreatment. Before testing catalytic activity, samples were heated at 773

TABLE 1

Catalysts and Their Features

Catalyst[a]	Cr content (wt %)	SA[b] (m^2g^{-1})	Pore radius (nm)	Surface Cr (at. nm^{-2})
ZrO_2(383)		121	1.7	
ZrO_2(923)B		32		
ZC0.9(383)B	0.88	176	1.7	0.68
ZC1.7(383)B	1.68	172		1.44
ZC0.5(923)B	0.51	39	5.5	1.53
ZC0.5(923)B*	0.52	32	9.0	1.90
SC3	3.15	220		1.71

[a] ZC0.5(923)B and ZC0.5(923)B* are distinct preparations from the same hydrous zirconia batch.

[b] After standard oxidation, not changed after reaction or redox cycles.

K in a flow of dry oxygen for 0.5 h (*standard oxidation*, s.o.). After cooling to 383 K and evacuation at the same temperature for 0.5 h, samples were treated with CO or H_2. The reduction was carried out to the desired extent in the circulation apparatus at various temperatures in the range 383–623 K, with subsequent outgassing at the reduction temperature for 10 min, and then at 623 or 723 K for 0.5 h. A trap placed downstream from the reactor was kept at 77 K to condense the released CO_2 (or H_2O). The extent of CO (or H_2) consumed in the reduction was calculated from the pressure decrease. At the end of reduction, the amount of CO_2 (or H_2O) was determined by measuring the pressure after expanding the condensate into a known volume. From the above quantities ($CO–CO_2$ or $H_2–H_2O$), the extent of reduction, expressed as e/Cr = (moles of electrons/moles of Cr), was calculated. Extents of reduction determined from the CO consumed $(e/\mathrm{Cr})_{\mathrm{CO}}$ were found to be systematically higher (10%) compared to those determined from the CO_2 produced $(e/\mathrm{Cr})_{\mathrm{CO_2}}$. This finding, already reported in Part I (*12*), can be attributed to the fact that $(e/\mathrm{Cr})_{\mathrm{CO}}$ represents an upper limit because CO consumption also includes the fraction of CO chemisorbed on zirconia without the reduction of Cr. On the other hand, $(e/\mathrm{Cr})_{\mathrm{CO_2}}$ represents a lower limit, since a fraction of CO_2 is irreversibly adsorbed on ZrO_2 sites (O^{2-}, OH^-) yielding stable-surface carbonate species which do not decompose by heating *in vacuo* at 623 or 723 K (*16*, *17*). Unless otherwise specified, the extents of reduction reported in this paper are $(e/\mathrm{Cr})_{\mathrm{CO_2}}$. When H_2 instead of CO was used as a reducing agent, less than 50% of the produced water was released at 623 K. Therefore, in the case of reduction with H_2, e/Cr values were calculated from the H_2 consumed, $(e/\mathrm{Cr})_{\mathrm{H_2}}$.

Extents of reduction and average oxidation numbers, $\bar{n}$, measured in the catalytic experiments are in very good agreement with those reported in Parts I and II (*12*, *14*). It is recalled that $\bar{n}$ is $\simeq$ 5.5 after s.o. and $\simeq$ 2.5 after reduction with CO at 623 K (*12*). This last treatment is designated hereafter as *standard reduction* (s.r.). Sequences of s.o. and s.r. are referred to as standard redox cycles.

Activity measurements: Circulation. A reactant mixture containing H_2 and C_3H_6 (molar ratio 4 : 1 at a total pressure of about 6.5 kPa) was circulated over the previously activated catalyst, maintained at the desired temperature (195 to 273 K). At the appropriate intervals (5 to 30 min) a small volume of gas (1.7 cm^3) was withdrawn and analyzed by GC. The decrease in pressure due to the reaction was also monitored. The efficiency of the circulation pump was tested by changing the reaction volume (0.15 or 0.5 liter).

When this was done, absolute kinetic constants (k_{abs}/ms^{-1}) (7), calculated assuming first-order dependence on H_2 pressure, did not show significant variations at a given temperature. The check indicates that the flow capacity of the circulation pump was sufficiently high to prevent limiting effects on reaction rates.

At a fixed e/Cr value, a simple evacuation at room temperature (RT) for 15 min between runs was sufficient to obtain reproducible activities. When passing to different extents of reduction (in a random sequence), catalysts were given a pretreatment consisting of s.o., reduction with CO (or H_2), and evacuation at 623 K.

Catalytic activities are expressed as initial rates (r_0/molecules s^{-1}) calculated at t = 0 from the slope of curves: molecules of propane vs time. To compare catalysts of different chromium content, activity data were also calculated as turnover frequencies per total Cr atoms, as N_{Cr} = r_0/total Cr atoms (N_{Cr}/mol s^{-1} at.$^{-1}$).

Activity measurements: Flow. Experiments were carried out in the temperature range 195 to 323 K. After activation, the sample was first treated in a flow of pure H_2 at the reaction temperature for about 5 min and subsequently exposed to the reactant stream consisting of 95% H_2 and 5% C_3H_6 (vol%). The mixture was flowed through the catalyst at a rate of 20 to 170 cm^3 min^{-1} and at a total pressure of abut 102 kPa. The reaction was generally followed for 1 to 3 h (in some cases up to 44 h) with a first analysis after 5 min, and then after every 15–20 min of reaction. During time on stream some deactivation was observed, probably due to polymeric or carbonaceous species strongly held on the surface of the catalyst. Therefore, activities were expressed as initial rates r_0 (mol s^{-1}) calculated at t = 0 from the equation $\ln r = \ln r_0 - \alpha t$, in which α is the deactivation coefficient and t is the time on stream. The equation satisfactorily fits experimental data, provided that conversions did not exceed 50%.

Because of the deactivation of the catalyst, in order to obtain reproducible activities in flow experiments, it was necessary to repeat s.o. and reduction (with e/Cr chosen at random) between runs. N_{Cr} values were calculated as for the experiments in circulation.

Other measurements. BET surface areas and pore-size distributions were determined by N_2 adsorption and desorption at 77 K as reported in detail in Part I. Chemisorption experiments, poisoning tests with CO, O_2, and CO_2 and other treatments to be specified were also carried out in the same apparatus as used for the catalytic measurements.

Gases

High purity hydrogen (SIO 99.999%) and propene (Matheson C. P.), used in flow experiments, were passed through commercial purifiers (Matheson model 6406). For circulation experiments hydrogen was previously passed through activated charcoal at 77 K, while propene was doubly distilled and the middle fraction was used. Oxygen (SIO 99.95%) was dried through magnesium perchlorate. CO (SIO 99.995%) was used without further purification.

RESULTS

Catalytic activity of CrO_x/ZrO_2

The results of the experiments in the circulation apparatus are reported first. The data are presented as an Arrhenius plot (log r_0 vs $1/T$) for ZC catalysts activated by s.o., followed by reduction with CO to various extents (e/Cr = 0.3 to 3.1 corresponding to $\bar{n} \simeq 5.2$ to 2.4), plus evacuation at 623 K (Fig. 1). The plot also shows the catalytic activity of pure ZrO_2 activated by evacuation at two temperatures (623 and 873 K) and, for comparison, the catalytic activity of pure ZrO_2, measured by Bird *et al.* (*18*). The following points are noticed:

(i) pure ZrO_2 is much less active than reduced CrO_x/ZrO_2 catalysts. The activity of the matrix is increased by increasing the heating temperature in vacuum. A good agreement is found between our data on pure ZrO_2 evacuated at 873 K and those reported by Bird *et al.* (*18*) on a ZrO_2 sample evacuated at the same temperature;

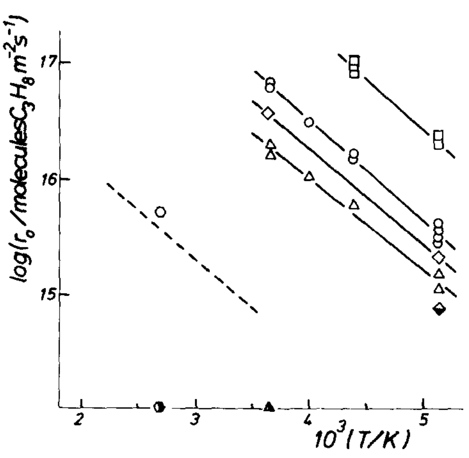

FIG. 1. A plot of log r_0 vs $1/T$ (data from circulation experiments). ZC0.5(923)B* reduced with CO to various extents: (○) e/Cr = 3.1, (□) e/Cr = 2.1, (△) e/Cr = 1.0, and (▲) e/Cr ≤ 0.3. ZC0.9(383)B: (◇) e/Cr = 2.8 and (◆) e/Cr = 3.1. ZrO_2 evacuated at different temperatures: (◑) 623 K, (○) 873 K, and (dotted line) activity level of ZrO_2 evacuated at 873 K, data from Ref. (*18*).

(ii) the apparent activation energy (E_a) of reduced ZC catalysts is 16 ± 1 kJ mol^{-1} and is independent of the extent of reduction, throughout the whole range from e/Cr = 0.8 to 3.1;

(iii) the catalytic activity of the ZC specimens markedly rises with increasing the extent of reduction. The dependence of the activity on the extent of reduction is somewhat complex, as indicated by the presence of a maximum, though not strongly marked, at e/Cr ≃ 2.1 ($\bar{n} \simeq 3.4$).

The dependence of activity on the extent of reduction. This aspect was investigated in two different ways. In *procedure A*, after s.o., samples were reduced with CO (or H_2) to various extents in random sequence before testing the catalytic activity. In *procedure B*, after s.o. and s.r., samples were reoxidized by stepwise addition of small amounts of oxygen at RT. Each addition of oxygen was adjusted to give an increase of $\bar{n} \simeq 0.1$. At all stages ESR spectra were recorded before testing the catalytic activity. The ESR results, as already mentioned in the Introduction, were in full agreement with those reported in Ref. (*14*). After both procedures the catalytic activity was measured at 195 K in the flow apparatus.

The results obtained with procedure A are illustrated first and are reported for various ZC catalysts as a plot of log N_{Cr} as a function of e/Cr or $\bar{n}$ (Fig. 2). The following main points emerge:

(i) a sharp increase in activity (2 to 3 orders of magnitude) is observed when the extent of reduction is increased from e/Cr = 0 to about 2.5 ($\bar{n}$ = 5.5 to 3). Upon further reduction, some decrease in catalytic activity is noticed. Specifically, after s.r. and at the maximum extent of reduction (e/Cr ≃ 3.1, $\bar{n} \simeq 2.4$), the N_{Cr} values are 3 to 5 times lower than those corresponding to the maximum activity;

(ii) no substantial difference is found when H_2 is used as reducing agent instead of CO. About the same maximum N_{Cr} and e/Cr values are in fact obtained by reducing the catalysts with either gas;

(iii) the catalytic activity is higher when

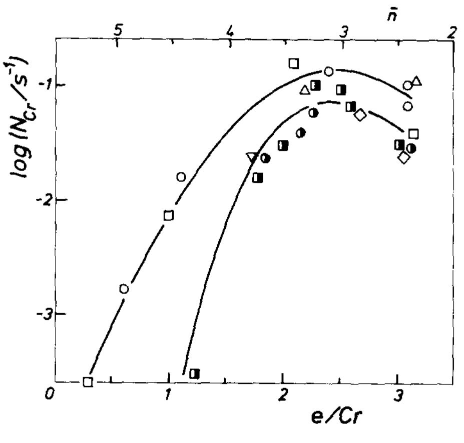

FIG. 2. Turnover frequencies per total chromium atoms (N_{Cr}/molecules s^{-1} at.$^{-1}$) at 195 K as a function of extent of reduction (e/Cr). The average oxidation number of Cr ($\bar{n}$) is reported also. Upper curve: ZC0.5(923)B*, (○) reduced with CO and evacuated at 723 K (flow), (□) reduced with CO and evacuated at 623 K (circulation). Lower curve: (◑) ZC0.5(923)B*, reduced with CO and evacuated at 623 K, (◧) ZC0.5(923)B reduced with CO and evacuated at 623 K (flow). (△) ZC0.5(923)B, reduced with H_2 and evacuated at 623 K, (▽) ZC0.9(383)B reduced with CO at 473 K and evacuated at 623 K (flow), (◇) ZC0.9(383)B, reduced with CO and evacuated at 623 K (circulation).

the temperature of evacuation after reduction with CO is increased from 623 to 723 K, especially at lower extents of reduction;

(iv) a satisfactory agreement between N_{Cr} values from flow and from circulation experiments is obtained. This can be seen in Fig. 2, where normalization for the differences in pressure was made, assuming first and zero orders with respect to H_2 and propene, respectively. It should be noted that there are appreciable differences in experimental conditions between the two sets of experiments; in particular, note the difference in the activation procedure between runs and the large difference in the mass of catalyst (0.3 g in flow experiments and 0.05 g in circulation experiments). The agreement indirectly shows the reliability of the method adopted to calculate r_0 values in flow experiments.

The results obtained with procedure B are examined next (Fig. 3). The stepwise addition of oxygen does not affect the activity of s.r. samples when e/Cr is progressively reduced from 3.1 to e/Cr $\simeq$ 2 ($\bar{n}$ increases from 2.4 to about 3.5). With the subsequent addition of oxygen, N_{Cr} values are found to decrease substantially. At $\bar{n}$ = 4.7, the activity is 2 orders of magnitude lower as compared to the maximum activity. It is remarkable that N_{Cr} values obtained with procedure B are seen to satisfactorily fit the same curve (log N_{Cr} vs e/Cr) obtained with procedure A (dotted line in Fig. 3). The N_{Cr} values reported in the e/Cr range 3.1 to 2 (points marked with an arrow in Fig. 3) are lower limit values since conversions were too high for an accurate evaluation of r_0. In these experiments, in fact, a larger mass of catalyst had to be used in order to have a reliable measurement of oxygen uptake.

The effect of H_2O vapor. This was studied on ZC catalysts reduced to the maximum extent by H_2 at 623 K and thereafter reacted with H_2O vapor (1.3 kPa) at various temperatures. The results relative to the ZC0.5(923)B sample are collected in Table 2. The data show that the catalytic activity is unaffected if the sample, after s.o. and reduction with H_2, is reacted with H_2O at either 723 or at 873 K. After reaction with H_2O at a higher temperature (1023 K), catalytic activity was substantially lower ($\simeq$5 times) but not suppressed. After the latter treatment, the catalytic activity was, however, completely restored by s.o. treatment followed by reduction at 623 K. It is noticed that after heating with H_2O at this high temperature (1023 K) the $(e/\text{Cr})_{H_2}$ value, determined by subsequent reduction with H_2, was substantially lower (2.2 instead of 3.1), thus suggesting some clustering of chromium.

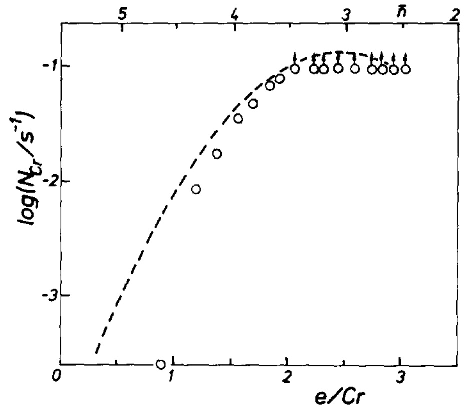

FIG. 3. Turnover frequencies per total chromium atoms (N_{Cr}/mol s^{-1} at.$^{-1}$) at 195 K as a function of extent of reduction (e/Cr). In the upper abscissae the average oxidation number of Cr ($\bar{n}$) is reported also. Catalyst ZC0.5(923)B* reduced with CO at the maximum extent (s.r., e/Cr = 3.1), evacuated at 723 K, and successively oxidized by stepwise addition of small quantities of oxygen at RT. The dotted line is the curve of Fig. 2 relative to the same sample reduced with CO and evacuated at 723 K. The arrows indicate lower limits.

Deactivation of the catalysts. The deactivation of the ZC catalysts and the ability to recover their initial activity were studied in both the circulation and flow apparatus. Kinetic results give no evidence of a deactivation in the whole T range from 195 to 273 K during experiments performed in the circulation apparatus. Some deactivation, as mentioned above under Procedure, was observed during catalytic experiments in flow. In a typical experiment at 195 K, the conver-

TABLE 2

The Effect of Heating in H_2O Vapor on Catalytic Activity

Treatments[a] (in sequence)	e/Cr[b]	SA (m^2g^{-1})	$N_{Cr} \times 10^2$ ($\text{mol s}^{-1}\text{ at.}^{-1}$)
s.o., H_2 at 623 K	3.1	39	10.7
As above plus H_2O at 723 K		39	10.7
s.o., H_2 at 623 K, H_2O at 873 K	3.0	34	8.5
s.o., H_2 at 623 K, H_2O at 1023 K	3.0	30	1.8
s.o., H_2 at 623 K	2.2	30	9.1

[a] Standard oxidation (s.o.) consists of heating with O_2 at 773 K. After heating in H_2O vapor at a given temperature, samples were evacuated for 0.5 h at the same temperature.

[b] Extent of reduction calculated from the amount of hydrogen consumed.

sions were 13.5% after 5 min, 9.3% after 2 h, 5.2% after 20 h, and 4.5% after 44 h. At a higher temperature the deactivation was more marked. In all cases, the initial activity was completely recovered after s.o. plus reduction with CO or H_2.

Dependence of activity on the support texture. The average pore size of ZCx(383) catalysts is substantially smaller as compared to that of ZCx(923) catalysts (Table 1). Whereas the activity of ZCx(923) was reproducible, that of ZCx(383) catalysts was much less so and generally 5 to 10 times smaller than that of ZCx(923). To some extent, the activity of ZCx(383) depends on the rate of reduction and on the final temperature of reduction. Specifically, within the ZCx(383) system higher activities were found when catalysts were slowly reduced (5 h instead of 0.5 h) at lower temperature (473 K instead of s.r.). The catalytic data relative to ZCx(383) samples reported in Figs. 1 and 2 are maximum activity values. It is seen that the latter values are close to those of ZCx(923) catalysts. The activation energy for the two sets of catalysts is nearly the same ($E_a = 16 \pm 1$ kJ mol^{-1}, Fig. 1).

Catalytic Activity of CrO_x/SiO_2

The catalytic activity of CrO_x/SiO_2 for the hydrogenation of propene has been extensively studied by Wittgen *et al.* (*6*) on well-characterized specimens. Some new experiments were carried out by us on an SC 3 catalyst activated by the same procedure adopted for ZC catalysts in order to have directly comparable activity data. In particular, after s.o. and s.r. treatments, the extent of reduction $e/Cr = 4.0$ was measured on SC 3. The latter value, corresponding to $\bar{n} = 2$, points to complete reduction of Cr(VI) to Cr(II), as previously reported for other CrO_x/SiO_2 reduced with CO (*19*). The catalytic activity at 195 K was $N_{Cr} = 2.51 \times 10^{-3}$ molecules s^{-1} $atom^{-1}$. Nearly the same activity was observed in another experiment in which the reduction with CO was stopped at $e/Cr = 2.7$ ($\bar{n} = 3.3$). When H_2 instead of CO was used as reducing agent, two important differences were observed: (i) the maximum extent of reduction was limited to $e/Cr = 3.1$ ($\bar{n} = 2.9$), and (ii) the N_{Cr} value at 195 K was substantially higher, $N_{Cr} = 1.00 \times 10^{-2}$. In another experiment, after s.o. and s.r. ($\bar{n} = 2$), the sample was heated in water vapor for 1 h at 773 K and evacuated at the same temperature before testing catalytic activity. After this treatment, N_{Cr} was 1.25×10^{-3} at 195 K. The ESR spectrum of this last catalyst showed the presence of some segregated α-Cr_2O_3.

DISCUSSION

On the basis of the catalytic results and the previously reported investigations on the chromia/zirconia system (*12–15*), two main points are discussed: (A) The oxidation number and the state of dispersion of the Cr active species and (B) the role of the matrix in comparison with SiO_2 and Al_2O_3.

A. Oxidation Number and Dispersion of the Active Species

The results allow identification of Cr(III) as the oxidation state involved in the active site, as pointed out by the following considerations:

(i) ZC catalysts must be reduced in order to be active, and therefore Cr(VI) and Cr(V) can be ruled out, leaving Cr(III) and Cr(II) as possible candidates.

(ii) After reaching the maximum Cr(III) concentration ($\bar{n} = 3.0$), a constant or a slightly declining activity upon further reduction is observed in the range where more Cr(II) is being formed ($\bar{n}$ from 3.9 to 2.5) (Fig. 2).

(iii) Any role of Cr(II) is also ruled out by the observation that heating the reduced catalyst ($\bar{n} = 2.5$) with water vapor up to 873 K, a process which destroys Cr(II) (*12, 14*), leaves the catalytic activity practically unchanged. The same argument also excludes any role of Cr(II)–Cr(III) pairs.

(iv) The stepwise addition of O_2 at RT to a catalyst previously reduced to $\bar{n} = 2.5$ does not affect its catalytic activity in the initial range of controlled oxidation up to $\bar{n} = 3.5$. Upon further oxidation from $\bar{n} = 3.5$ to $\bar{n} = 4.7$, the activity strongly decreases.

(v) The E_a value is practically constant over a wide e/Cr range, thus suggesting that the same active site is operating over the whole range.

Having now focused on Cr(III) as the active oxidation state, the catalytic results together with the ESR and IR findings show that not all Cr(III) species are equally active, as discussed below.

The ESR analysis has shown that two Cr(III) species (different from α-Cr_2O_3) can be distinguished: Cr(III)-δ and Cr(III)-β. The δ species is preferentially formed upon CO reduction of Cr(V); it is mononuclear, and is not affected by H_2O treatment up to about 873 K. The catalytic activity is high in all states of the catalyst where this species is identified. The β species is formed from the selective oxidation of Cr(II) with water. The ESR analysis shows that it corresponds to a more magnetically concentrated species than δ. The catalytic behavior of the two species appears different. In fact,

(a) when a reduced ($\bar{n} = 2.5$) catalyst is subjected to selective oxidation with water, the overall Cr(III) concentration is increased, but the β-species is now formed, leaving the δ-species unchanged; no increase in catalytic activity is observed, and

(b) in the early stages of reduction from $\bar{n} = 5.5$, Cr(III) is being formed, as identified by IR (*13*) but although not yet seen by ESR, which requires a weakly interacting species for its detection. In this range, the catalytic activity is steeply increasing.

In condensed fashion, the arguments illustrated above are represented in Fig. 4, which reports the $\bar{n}$ values ensuing from the different treatments as a bar diagram, with the actual species and the techniques leading to their identification in the underlying numbered boxes, and, by means of stippled areas within the bars, those states of the catalyst which were found to be active.

We conclude that the catalytically active species must be sought among the Cr(III) species belonging to isolated or weakly interacting population. However, not necessarily all of these species are equally active. In fact, the very difference between Cr(III)-δ and Cr(III)-β focuses attention not merely on the oxidation state of Cr, but also on its coordination and on its ligand sphere of interaction. A high coordinative unsaturation, such as is more likely to be present for isolated or nearly isolated Cr(III) species, is therefore suggested.

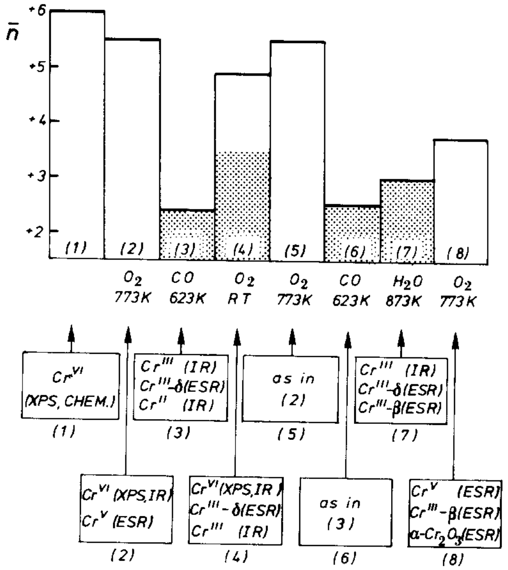

FIG. 4. Average oxidation number ($\bar{n}$), catalytic activity, and relevant Cr species of CrO_x/ZrO_2 catalysts after different treatments. Numbered boxes specify the Cr species and the identification techniques. Stippled areas indicate high catalytic activity. After O_2 treatment the activity strongly decreases at $\bar{n} > 3.5$.

Active fraction of Cr(III) species. An estimate of the upper limit for the active fraction of Cr(III) can be obtained from the stepwise addition of oxygen experiments to the s.r. ZC0.5(923)B* catalyst (Results, procedure B). After s.o. (state 2 of Fig. 4), Cr(VI) and Cr(V) are present on the surface of the ZC0.5(923)B* in about equal amounts ($\bar{n}$ = 5.5). After s.r. (state 3 of Fig. 5), Cr(III) and Cr(II) are formed from the reduction of Cr(V) and Cr(VI), respectively, in about equal amounts ($\bar{n}$ = 2.5). In the controlled oxidation process at RT (steps 3 to 4, in Fig. 4), Cr(VI) from Cr(II), on IR evidence (*13*), is preferentially and reversibly restored, whereas Cr(V) from Cr(III), on ESR evidence (Part II), is only partially restored. At $\bar{n}$ = 4.7, when the catalytic activity is suppressed (Fig. 3), the surface composition of chromium, expressed as molar fraction $x_{(N)}$, can be calculated from

$$\bar{n} = 6x_{(VI)} + 5x_{(V)} + 3x_{(III)}$$

In the latter expression, at $\bar{n}$ = 4.7, the molar fraction of Cr(VI) is $x_{(VI)} = 0.5$, since all Cr(II) has been oxidized to Cr(VI) (remember that $x_{(II)} = 0.5$ in the s.r. sample), and $x_{(III)} + x_{(V)} = 0.5$, since Cr(III) has been only partially oxidized to Cr(V) (remember that $x_{(III)} = 0.5$ in the s.r. sample). Accordingly, $4.7 = 6 \times 0.5 + 5\,(0.5 - x_{(III)}) + 3\,x_{(III)}$, from which $x_{(III)} = 0.4$ and $x_{(V)} = 0.1$ are calculated.

An alternate way to check the $x_{(N)}$ values is to derive them from the ESR determination of Cr(V). On the above sample, at $\bar{n}$ = 4.7, the measured Cr(V) intensity was 13% of the maximum Cr(V) signal intensity, when $x_{(V)}$ was 0.5 ($\bar{n}$ = 5.5). By the same arguments as before, this gives $x_{(V)} = 0.5 \times 0.13 = 0.065$ and hence $x_{(III)} = 0.50 - 0.065 = 0.435$, from which $\bar{n}$ is calculated as $6 \times 0.5 + 5 \times 0.065 + 3 \times 0.435 = 4.63$, which is in reasonable agreement with the experimental value (4.7). The two checks agree on the indication that the activity is lost when 13% (ESR) or 20% (from $\bar{n}$-values) of the original Cr(III) present in s.r. state is oxidized. As Cr(III), at $\bar{n}$ = 2.5, was about 50% of the total Cr, an upper limit of 6.5 to 10% of total Cr for the active fraction is obtained.

The nature of the active Cr(III) can now be better specified. As mentioned above, Cr(III) is formed in the early stages of the reduction, when IR spectra (*13*) clearly show its formation and catalysis registers a marked increase of activity. When the reduction proceeds, weakly interacting Cr(III) species (Cr(III)-δ) are detected by ESR (*14*) and catalysis registers a constant or slightly decreasing activity. These facts suggest that the active Cr(III) ions are the species formed in the early stages of the reduction and arise from mononuclear, isolated Cr(V) species. The statement that the Cr(III) ions detected by ESR in the later stages of reduction as Cr(III)-δ (9 to 18% of total Cr, Table 3 of Part II) do not contribute to the activity, also accounts for the less reproducible behavior and lower activities measured in some of the experiments on ZCx(383) as compared to

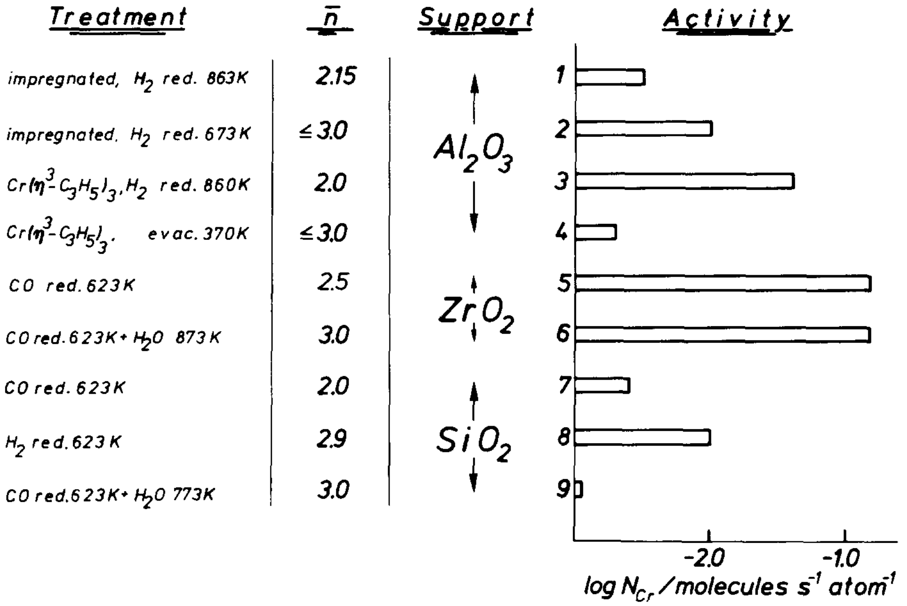

FIG. 5. Turnover frequencies per total Cr atoms (N_{Cr}) of Cr supported on Al_2O_3, ZrO_2, and SiO_2. Reduction treatments and relevant $\bar{n}$ values are as specified. N_{Cr} values of Cr supported on Al_2O_3 are calculated from the data of Ref. (*5*).

ZC*x*(923) samples. A higher tendency toward the formation of Cr(III)-δ species was in fact observed on the former catalysts as compared to the latter (*14*).

B. The Role of the Support

The catalytic activity of CrO_x/ZrO_2 for propene hydrogenation is now compared with that of CrO_x/SiO_2. The comparison can be extended to the CrO_x/Al_2O_3 system, taking the data reported by Iwasawa (*5*), who studied both the conventionally impregnated CrO_x/Al_2O_3 samples and Cr anchored on Al_2O_3 catalysts prepared by reacting the $Cr(\eta^3-C_3H_5)_3$ complex with previously activated alumina (referred to as Cr(II)-anchored or Cr(III)-anchored catalysts).

Turnover frequencies at 195 K calculated with respect to the total Cr content (N_{Cr}/mol s^{-1} at.$^{-1}$) for the various Cr-supported catalysts are reported in Fig. 5, where the various reduction procedures, the relevant $\bar{n}$-values, and the support are also specified. Catalysts of not very different surface chromium content (0.6 to 1.9 Cr atoms nm^{-2}) and activation energies E_a are compared. E_a values are all in the range 15 to 16 kJ mol^{-1} for the CrO_x/ZrO_2, CrO_x/SiO_2, and Cr anchored on alumina catalysts, and 23 kJ mol^{-1} for the impregnated CrO_x/Al_2O_3 (*5*). For all catalysts, activities have been measured at 195 K except for the impregnated CrO_x/Al_2O_3, for which the 195 K values were extrapolated from those at 230 K (*5*). Data show that the reduced CrO_x/ZrO_2 catalyst ($\bar{n}$ = 3) is about 3.6 times more active than the Cr(II) anchored on Al_2O_3 catalyst and 1 to 2 orders of magnitude more active than all other chromium-supported systems. However, an important difference emerges between the Cr(II)-anchored catalyst and the reduced CrO_x/ZrO_2. The activity reported in Fig. 5 for the Cr(II)-anchored catalyst is a maximum activity value, which refers to a sample not submitted to redox cycles. A considerable decrease in activity, not quantified by the author (*5*), is observed when the Cr(II)-anchored sample is submitted to redox cycles with oxygen and hydrogen. As mentioned by Iwasawa (*5*), after repeated redox cycles not only does the activity decrease but also the extent of the coordinative unsaturation on the Cr(II) active site decreases. In contrast to the behavior of the Cr(II)-anchored catalyst, it is stressed that the activity of the reduced ZC samples remains high and constant after several standard redox cycles. In one case, as many as 30 cycles were performed on the same ZC catalyst without observing a decrease of activity.

The finding that chromium supported on ZrO_2 is substantially more active than on other supports points to the role of the matrix. The matrix not only affects the extent of coordinative unsaturation on chromium and the stabilization of specific oxidation states of Cr, but it can also enter directly in the structure of the active site by participating in kinetically important steps, such as the heterolytic dissociation of the dihydrogen molecule on chromium–oxygen sites. Inspection of Fig. 5 shows that (i) Cr(III) on ZrO_2 and SiO_2 (see bars 6 and 8) is more active than Cr(II) on the same matrices (see bars 5 and 7), (ii) Cr(II) anchored to Al_2O_3 is also very active (see bar 3), and (iii) both Cr(II) and Cr(III) are almost inactive when the reduction procedure adopted for their formation favors the clumping of chromium (repeated redox cycles for the Cr(II) anchored on Al_2O_3, and reduction *plus* reaction with H_2O for the Cr(III) on SiO_2 catalyst). All these facts show that both Cr(II) and Cr(III) possess electronic configurations which are suitable for yielding very active catalysts but that the electronic structure alone does not guarantee a high catalytic activity. The coordinative unsaturation on the active site appears to be an additional and essential factor. Whereas the relevance of the two factors has been widely recognized in previous investigations, the fact that electronic structure and coordinative features must both be simultaneously suitable for a high catalytic activity should not be overlooked and is a key to the apparently contradictory results and to the long debates concerning the active oxidation state of chromium.

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