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Propane Dehydrogenation on Chromia/Silica and Chromia/Alumina Catalysts

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The catalytic activity of CrO_x/SiO_2 (SC, 0.08 to 0.99% chromium by weight), CrO_x/Al_2O_3 (AC, 0.16 to 1.55%), and α-Cr_2O_3 for the dehydrogenation of propane has been investigated at 723 to 823 K in a flow apparatus. Before catalytic experiments, SC and AC samples were activated with oxygen at 773 K (s.o. treatment) followed or not followed by reduction with CO or H_2 at 623 K. Occasionally, SC samples were dehydrated under vacuum at 1023 K before the s.o. treatment. Assuming all chromium to be in the +6 state after s.o., the average oxidation number of chromium ($\bar{n}$) is $\bar{n} \simeq 2$ in SC samples reduced with CO and $\bar{n} \simeq 3$ with H_2. In AC catalysts, $\bar{n}$ values progressively increase in consecutive reduction experiments, from $\bar{n} = 2.2$ to $\bar{n} = 4.2$. All catalysts are highly selective to propene and undergo a deactivation process during time on stream. The s.o. treatment completely restores the activity. The reduction mode does not influence the catalytic activity. Surface species formed upon adsorption at room temperature (RT) of CO or NO were studied by IR spectroscopy on CrO_x/SiO_2 submitted to treatments analogous to those used before catalytic experiments. In SC catalysts reduced with CO, the formation of carbonyls and nitrosyls of three different Cr^{II} species was confirmed. Interestingly, all these species were absent when the sample was (i) reduced with H_2 at 773 K, or (ii) heated with H_2O after reduction with CO, or (iii) exposed to propane after reduction with either CO or H_2. After treatments (i) through (iii), a carbonyl and a dinitrosyl of Cr^{III} were the only species formed on CO or NO adsorption at RT. Relying on (i) the dependence of the activity on chromium content, (ii) IR results, and (iii) ESR data, it is suggested that mononuclear Cr^{III} with two coordinative vacancies is the active site for the dehydrogenation of propane. The catalytic activity of CrO_x/SiO_2, CrO_x/Al_2O_3, and α-Cr_2O_3 is compared with that of CrO_x/ZrO_2, measured previously. Possible reasons for the substantially higher activity of CrO_x/ZrO_2 are discussed.

INTRODUCTION

The activity and selectivity of supported chromia catalysts for the dehydrogenation of light alkanes have been known for many decades (1, 2). Widely employed industrial catalysts for this reaction are chromia supported on γ-Al_2O_3 modified by addition of alkali ions (often potassium). On the other hand, the problem of identifying (i) the oxidation state and (ii) the coordinative unsaturation features of active chromium is still open. We refer to the work by Lugo and Lunsford (3) for a comprehensive list of investigations directed to identifying the chromium active site. To gain a better knowledge of points (i) and (ii), the study of chromium on various supports is a convenient approach. General reasons for studying the activity of chromium on various supports, and in particular the interest of investigating these catalysts in reactions such as hydrogenation and dehydrogenation, have been illustrated in previous work (4–7). Within this framework an investigation of the catalytic activity of CrO_x/ZrO_2 (ZC) for the dehydrogenation of propane has been recently reported (8). The system was found to be highly active and selective in the dehydrogenation of propane at 723–823 K. The surface composition of the catalyst (nature of chromium species) and therefore its catalytic activity were found to be mainly controlled by the reaction atmosphere. That is to say, it was found that the mode of catalyst reduction is not important at the high temperature of propane dehydrogenation. The authors concluded that mononuclear Cr^{III} species are the active sites with a possible role of the oxide ions next to Cr^{III} (8). In contrast, Lugo and Lunsford (3), in an investigation of ethane dehydrogenation over chromium catalysts, stated that Cr^{II} species with three coordinative vacancies are the active sites for the reaction.

The present paper reports (i) the catalytic activity of CrO_x/SiO_2 (SC), CrO_x/Al_2O_3 (AC), and α-Cr_2O_3 catalysts for the dehydrogenation of propane, (ii) the characterisation of SC and AC catalysts by means of redox cycles with O_2–CO (or H_2)–O_2, (iii) a FT-IR study of chromium species identified by adsorption at room temperature (RT) of CO or NO on SC catalysts, and (iv) an ESR characterisation of AC samples. Reference is made to previous

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characterisation by ESR and/or IR of ZC (6, 9–12), SC (13–21), and AC (12, 21, 22) samples. The catalytic activity of SC, AC, and α-Cr_2O_3 samples is compared with that of ZC catalysts, which were previously investigated (8).

EXPERIMENTAL

Materials

The CrO_x/SiO_2 catalysts have been prepared by impregnation of SiO_2 Aerosil 300 (Degussa) or in one case (as specified) Cabosil (Cabot Corp.) with a titrated aqueous solution of CrO_3. After drying at 393 K, the samples were heated in oxygen at 773 K, as specified below.

The CrO_x/Al_2O_3 catalysts have been prepared by impregnation of γ-alumina obtained by decomposition of boehmite at 773 K with the aforementioned solution of CrO_3. After drying at 393 K, the samples were calcined in air at 773 K for 5 h.

The crystalline chromia was prepared by rapid addition of 150 ml of 1 *M* ammonia solution over 30 min to 700 ml of a chromium nitrate solution 0.07 *M* (23).

The CrO_x/SiO_2 and CrO_x/Al_2O_3 samples are designated as SC*x* and AC*x*, respectively, where *x* specifies the approximate chromium content (wt%). Measurements of surface area were carried out in the same apparatus employed for activity measurements with a standard volumetric BET method using nitrogen as adsorbate at 77 K. All catalysts investigated with some of their features are listed in Table 1. The reported surface areas are those measured after catalytic runs. For SC and AC catalysts the values are coincidental with those measured for "as prepared" or "after s.o." samples, where 's.o.' indicates treatment in oxygen at 773 K. The surface area of α-Cr_2O_3 decreased from 46 m^2g^{-1} for the "as prepared sample to 20 m^2g^{-1} after all catalytic runs.

Hydrogen (99.999%), propane (99.8), nitrogen (99.998), CO (99.995), and oxygen (99.995) were purchased from SOL; NO and helium (UHP) were obtained from Matheson. Propane was passed through commercial purifiers (Matheson Model 6406). CO for catalyst reduction was liquefied at 77 K, distilled, and the middle fraction was used. Oxygen was dried over magnesium perchlorate. NO was purified by repeated vacuum distillation at 145 K.

TABLE 1

Catalysts and Their Features

Catalyst	Cr content wt%	Surface area (m^2g^{-1})	Cr surface density (atoms nm^{-2})
SC0.08	0.078	296	0.03
SC0.05	0.46	287	0.19
SC0.9	0.90	285	0.37
SC1 (Cabosil)	0.99	166	0.69
AC0.16	0.16	184	0.10
AC0.6	0.62	176	0.41
AC0.8	0.85	203	0.49
AC1.6	1.55	184	1.00
α-Cr_2O_3		20	10.84[a]

[a] From Ref. 3.

Apparatus

The activity was measured in a flow apparatus at atmospheric pressure. The equipment has previously been described in detail (8). In essence, it is composed of two sections. The first is an all-glass vacuum line, with a circulation loop of volume 0.15 liter, equipped with an MKS Baratron pressure transducer (sensitivity 1 N m^{-2}) and a magnetically driven recirculation pump (flow rate = 0.8 liter min^{-1}) for catalyst conditioning and adsorption measurements. The second part is a flow section for catalytic runs. The catalyst (usually 0.5 g) in the form of powder was placed on a fritted disk sealed inside a silica reactor (12 mm internal diameter), which could be connected to the vacuum line or to the flow section by means of a four-way valve. The height of the catalyst bed was 5 to 10 mm. The reactor temperature was controlled within ±1 K by a commercial device. Isothermal conditions were approached by feeding the reactant diluted in an inert gas (see below). The analysis of reactants and products was carried out with a gas chromatograph (C. Erba GC 6000 Vega Series 2) with a column (2 m in length, 4 mm internal diameter) filled with silica gel 60–80 mesh and employing nitrogen as carrier gas. A temperature program from 343 to 403 K and a FID detector in series with a HWD detector were used. The system allowed the separation of hydrogen, methane, ethane, ethene, propane, and propene, in this order. The areas of the gas chromatographic peaks were evaluated by an integrator (Spectra Physics Model SP4290).

ESR measurements were made at RT on a Varian E-9 spectrometer operated at X-band frequencies. The spectrometer was equipped with an on-line computer for data treatment. For these experiments, a silica reactor equipped with a side ESR tube to which the catalyst could be transferred without exposure of the sample to the atmosphere was used.

IR spectra were run on an FT-IR spectrometer (Perkin–Elmer 1760-X) with a resolution of 2 cm^{-1}. The powdered samples were pelleted (pressure, 20×10^3 kg cm^{-2}) in self-supporting disks of ca. 100 mg cm^{-2} mm^{-1}, and put in an IR cell which allowed thermal treatments *in vacuo* or in a controlled atmosphere.

Procedure

Before reaction the catalysts were subjected to a standard oxidation (s.o.) in a flow of dry oxygen at 773 K for 0.5 h followed by evacuation for 0.5 h at 383 K. In some cases, to be specified, SC catalysts were dehydrated *in vacuo* at 1023 K for 2 h before the s.o. treatment. After s.o. the catalyst could be reduced or not reduced before the catalytic run. Reductions were carried out in circulation with CO or hydrogen at 423–623 K for 0.5 h after outgassing at 383 K for 0.5 h, or in a flow of hydrogen at 623–773 K after purging for 10 min with nitrogen at 773 K. When reduction was performed in circulation, the amount of the reducing agent (CO or H_2) consumed and the amount of the oxidation product released (CO_2 or H_2O) after outgassing at 723 K were measured. In the reduction with carbon monoxide, the amount of CO_2 released at 723 K is 10 to 15% less than the amount of CO consumed at 623 K. In the reduction with hydrogen, the water released at 723 K is only 50% of the hydrogen consumed at 623 K, the other 50% remaining adsorbed on the surface. The extent of reduction (e/Cr = electrons per chromium atom) could be determined as previously illustrated in detail (5). In the reductions with CO, the e/Cr determination could be based either on CO consumed or on CO_2 released, while in the reduction with H_2, the e/Cr calculation could only be based on the H_2 consumed, due to the large amount of water retained by the surface. In some experiments, the reduced catalyst was submitted to back-oxidation with O_2 at 773 K. The e/Cr values measured in the reduction with CO were in good agreement (±5%) with those measured in the reoxidation with O_2. Unless otherwise specified, the reported e/Cr values were calculated from the amount of reducing agent consumed (CO or H_2). Before the catalysis experiments were started, samples were always conditioned at the reaction temperature with flowing nitrogen for about 10 min.

Most of the dehydrogenation experiments were carried out with a reactant mixture containing 5% molar propane in N_2 with total flow rate of 20–200 ml min^{-1}.

Rates were evaluated as propene molecules leaving the reactor per second from experiments in which conversion did not exceed 50% of the equilibrium value. These rates represent average values along the catalyst bed. However, under the worst condition (50% of the equilibrium value), assuming first order reaction, the rate is underestimated by about 30% with respect to the rate at near-zero conversion. This maximum discrepancy is not significant when looking at large effects. The equilibrium conversion for a mixture which initially contains 5% molar propane in N_2, derived from standard free energies of formation and assuming ideal behaviour, are the following: 33, 54, and 75% at 723, 773, and 823 K, respectively. The absence of mass transfer limiting effects was established by evaluating the Thiele modulus (<0.5) and by varying the flow rate in a wide interval (20–200 cm^3 min^{-1}), as specified in a previous paper (8).

Usually the reaction was followed for 3 h, with a first analysis at 5 min from the start, and then about every 15 min. Deactivation with time on stream was observed in all cases due to deposition of coke. In some experiments, the amount of coke formed at various times on stream was determined by oxidation to CO_2 and H_2O with O_2 at 773 K. The deactivation was found to be nearly proportional to the amount of coke. Activities will be referred to the initial rates r_0 (C_3H_6 molecules s^{-1}), obtained by extrapolation to $t = 0$ from the expression $\ln r = \ln r_0 - \alpha t$, which satisfactorily fits the experimental data. 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 (molecules s^{-1} $atom^{-1}$).

The FT-IR experiments were carried out by adsorption of CO or NO at RT on the SC0.5 sample submitted to treatments analogous to those adopted before catalytic experiments. Before all experiments, the catalyst was first heated *in vacuo* by slowly increasing the temperature to either 773 or 1023 K, and subsequently evacuated at 773 K for 3 h. The sample was thereafter heated with O_2 (P = 40 Torr) at 773 K before a final evacuation at 623 K. Reduction with CO was carried out for 0.5 h at 623 K (P = 40 Torr) and was followed by evacuation for 5 min at the same temperature. This treatment is hereafter referred to as s-CO. Reduction with H_2 was carried out for 0.5 h at 773 K (P = 20 Torr) and was followed by evacuation for 0.5 h at the same temperature. This treatment is hereafter referred to as s-H_2. During reduction, CO or H_2 were changed every 10 min with fresh portions of gas, and the CO_2 or H_2O produced were condensed in a trap at 77 K placed in the vicinity of the IR cell.

RESULTS

Characterisation of Samples by Redox Cycles

The extent of reduction (e/Cr) measured by the CO or H_2 consumed at 623 K, $(e/\mathrm{Cr})_{\mathrm{CO}}$, and $(e/\mathrm{Cr})_{\mathrm{H_2}}$, respectively, are reported in Table 2 for some SC and AC catalysts. The e/Cr values have been determined from two types of experiment. In the first type, e/Cr values were measured from "reduction-catalysis-s.o." cycles (red.-cat.-s.o.), in the other one, from "reduction-s.o." cycles (red.-s.o.). In particular, in the (red.-cat.-s.o.) experiments, the sample after s.o. was (i) reduced with CO or H_2 at 623 K, (ii) used in a dehydrogenation catalytic run, and (iii) oxidised by s.o. In the case of the (red.-s.o.) experiments, the same procedure was adopted except for the fact that catalytic experiments were omitted in the cycle. For a given catalyst, e/Cr values refer to experiments performed in sequence as displayed, from top to bottom, in Table 2.

For the SC catalysts, the e/Cr values (Table 2) show a modest decrease in consecutive experiments. No substantial difference in the reducibility is observed when e/Cr values obtained by *either* the (red.-cat.-s.o.) *or* the (red.-s.o.) cycles are compared. Assuming all chromium to be

TABLE 2

The Extent of Reduction (e/Cr) Determined from the H_2 or CO Consumed at 623 K by Catalysts Previously Heated with O_2 at 773 K

	After reduction in reduction-catalysis-s.o. cycles[a,b]		After reduction in reduction-s.o. cycles[b,c]	
Sample	$(e/Cr)_{CO}$	$(e/Cr)_{H_2}$	$(e/Cr)_{CO}$	$(e/Cr)_{H_2}$
SC0.5	4.0		4.0	
	3.6		3.7	
		2.8	3.5	
	3.6			2.8
		2.9	3.6	
	3.6			
AC0.6	3.8		3.8	
	2.3		3.3	
	2.1		3.1	
		1.9		2.9
		1.8		2.4
AC1.6	2.9			
	2.3			
	2.0			
	1.8			

[a] After heating with oxygen at 773 K, the sample was: (i) reduced with CO or H_2 at 623 K, (ii) used in a dehydrogenation catalytic run, (iii) oxidised by s.o., and (iv) reduced again with CO or H_2.

[b] The e/Cr values refer to experiments performed in sequence as displayed, from top to bottom.

[c] The same procedure as in (a) was adopted except for the fact that catalytic experiments were omitted in the cycle.

in the +6 state after the s.o. treatment, an average oxidation number ($\bar{n}$) for chromium can be calculated as $\bar{n} = 6 - e/\text{Cr}$, after the various reduction treatments with CO or H_2. The $\bar{n}$ values, calculated according to this procedure from the e/Cr data of Table 2, give $\bar{n} = 2$ to 2.4 for the SC0.5 sample reduced with CO, and $\bar{n} = 3.1$ to 3.2 for the sample reduced with H_2.

In special experiments, after reduction with H_2 at 623 K, the sample was further heated with CO at the same temperature. From the amount of CO consumed in the latter treatment $(e/\text{Cr})_{CO} = 0.7$ to 1 was determined.

Unlike the findings for the SC samples, the e/Cr values for AC samples (Table 2) show a large decrease in consecutive experiments. Moreover, the reducibility measured in the (red.-cat.-s.o.) cycles is substantially lower in comparison to that measured in the (red.-s.o.) cycles.

ESR Results

The nature of chromium species on the surface of CrO_x/SiO_2 (19–21) and CrO_x/ZrO_2 (6, 12, 21) as investigated by ESR spectroscopy has been reported in the previous papers to which reference is made. The CrO_x/Al_2O_3 system has also been studied (21, 22). ESR results reported in the present paper refer to the AC system.

After the s.o. treatment, a broad and slightly asymmetrical ESR line is observed in all AC samples. Because of these unfavourable features, average g values ($g_{av} = 1.971$, g_{av} calculated from the field at the centre of the ESR line), and ΔH peak-to-peak ($\Delta H_{pp} = 52$ G) are the only parameters which can be evaluated from the ESR spectra. However, in a recent paper (21), by using also ^{53}Cr-enriched AC samples, it has been shown that the absence of resolved structure is well explained by assuming superhyperfine interaction (shf) of mononuclear Cr^{V} species with two equivalent ^{27}Al nuclei (slightly anisotropic shf 6 to 8.5 G). This fact demonstrates the existence in AC of the same mononuclear Cr^{V} species in a square pyramidal configuration identified previously in ZC and SC systems (6, 19–21).

After the s.o. treatment of AC samples, amounts of Cr^{V} corresponding to 9% and 8% of total chromium present in the sample were measured in AC0.6 and AC1.6, respectively. A slightly higher percentage of detectable Cr^{V} was previously measured in a more dilute sample (11% of total Cr detected as Cr^{V} in the AC0.06 sample (21). Upon reduction with either CO or H_2, the intensity of the signal from Cr^{V} is reduced to less than 10% of its initial value, and a broad signal, attributed to Cr^{III}, is observed ($g_{av} \simeq 2.2$ with a broad maximum at g in the range 3.8 to 5.0). The spectroscopic features of similar broad signals arising from Cr^{III} species have been discussed in previous papers (6, 20). Here, it is sufficient to recall that two main types of signals are obtained on reduction of chromia-supported systems. The first one is a very broad signal, designated the δ-signal, with $g_{av} \simeq 2.2$ and a broad maximum at g in the range 3.8 to 5.0. This signal, assigned to weakly interacting Cr^{III} ions, has been previously detected on reduced ZC (6) and SC (20) and also it has now been observed on reduced AC samples. The second signal (β-signal, $g_{av} = 1.98$ and $\Delta H_{pp} = 1500$ to 1800 G), not detected in the present investigation in AC samples, arises from a chromia-like phase formed when ZC samples were heated at high temperature with oxygen ($T \geq 973$ K), or with water vapour at $T \geq 773$ K after reduction with CO or H_2 (6).

In the AC samples, after the first reduction treatment with either CO or H_2, the Cr^{V} species can only be partially restored in the subsequent s.o. treatment (to 50% of its original value). In subsequent cycles, the amount of Cr^{V} which can be restored tends to level off. In a similar way, only a small fraction of Cr^{III} produced in the first reduction treatment can be reoxidised by a subsequent s.o. treatment. However, it is recalled that Cr^{III}-δ species of ZC (6) and SC (20) samples were reversibly oxidised after the s.o. treatment. The different behaviour in the case of AC samples suggests that Cr^{III}-δ species are less exposed on the surface of Al_2O_3, compared to SiO_2 and ZrO_2. On the whole, the AC system appears to be less reversible compared with SC and ZC catalysts. The behaviour observed by ESR on AC samples, specifically the lack of full reversibility, accounts for the decrease of *e*/Cr values observed in redox cycles.

FT-IR Results

IR spectra obtained by adsorption of CO or NO at RT on the SC0.5 sample dehydrated at 1023 K and submitted to various treatments (to be specified) are reported in sections a and b, respectively, of Figs. 1 and 2. The results of analogous experiments performed on the SC0.5 sample dehydrated at lower temperature (773 K) are reported in Fig. 3.

The results obtained on samples dehydrated at 1023 K are illustrated first. The adsorption of CO at RT on the s-CO reduced sample (Fig. 1a, spectrum 1) leads to a triplet of bands at wavenumbers of 2190, 2184, and 2178 cm^{-1} at higher CO coverage ($P_{CO} \geq 2$ Torr), and a doublet (2190, 2180 cm^{-1}, spectra not shown) at lower CO coverage. The adsorption of NO at RT on the sample after the s-CO reduction (Fig. 1b, spectrum 1) gives bands at 1870, 1855, 1805, and 1742 cm^{-1} (the band at 1742 cm^{-1} arises from the overlapping of two slightly different components at 1741 and 1744 cm^{-1}). Nearly identical spectra, both with CO and NO, have been previously reported by Zecchina *et al.* (13–18) on CrO_x/SiO_2 catalysts reduced with CO using the same procedure adopted here. The analysis of these spectra, taken together with additional information attained on adsorption of an extra ligand (CO, pyridine, NH_3, and H_2O) on reduced catalyst with preadsorbed NO (24–26), has allowed us to identify in the s-CO reduced samples three distinct species of chromium. The average oxidation number of chromium in the s-CO sample used in IR experiments was $\bar{n} = 2.1$, as determined from the amount of oxygen consumed in a subsequent oxidation at 773 K. This finding suggested that a small fraction of chromium could be present as Cr^{III}, and therefore, in previous papers (13, 14, 24, 25), it was proposed that this Cr^{III} contributed to the IR spectrum. More recent studies (15–18, 26) allowed a reassignment of the IR bands which have been attributed to three distinct Cr^{II} species, designated $Cr^{II}(A)$, $Cr^{II}(B)$, and $Cr^{II}(C)$. The three species differ by the number of oxygen ligands to which chromium is coordinated and, consequently, by the extent of the

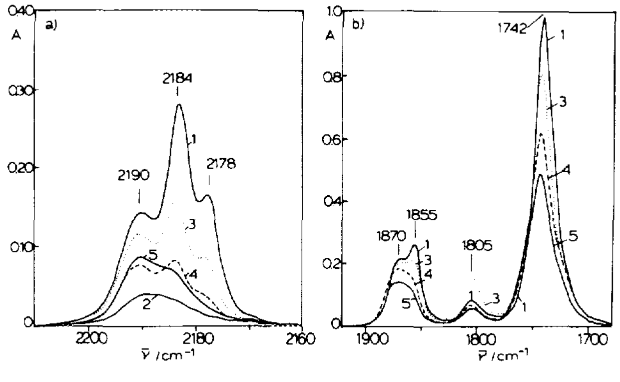


FIG. 2. FT-IR spectra of CO (section a) and NO (section b) adsorbed at RT on the SC0.5 sample. Before adsorption of CO or NO, the sample was first evacuated at 1023 K and then submitted to various treatments, as specified hereafter. Curve 1: reduction with CO (the same as in Fig. 6, reported for a comparison); curve 2: reduction with H_2 followed by heating in C_3H_8 at 773 K (20 Torr, 30 min) and evacuation at 773 K for 5 min; curve 3: reduction with CO followed by heating under vacuum at 773 K for 30 min; curve 4: reduction with CO followed by heating in H_2 at 773 K (20 Torr, 30 min) and evacuation at 773 K for 5 min; curve 5: reduction with CO followed by heating in C_3H_8 at 773 K (20 Torr, 30 min) and evacuation at 773 K for 5 min.

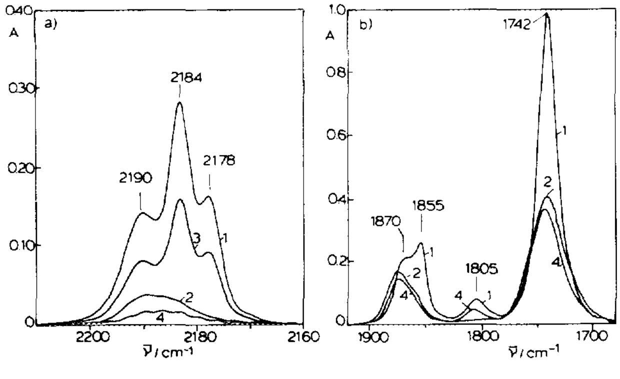


FIG. 1. FT-IR spectra of CO (section a) and NO (section b) adsorbed at RT on the SC0.5 sample. Before adsorption of CO or NO, the sample was first evacuated at 1023 K and then submitted to various treatments, as specified hereafter. Curve 1: reduction with CO; curve 2: reduction with H_2; curve 3: reduction with H_2 followed by reduction with CO; curve 4: reduction with CO followed by heating with water at 623 K (12 Torr, 30 min) and evacuation at 773 K for 30 min.

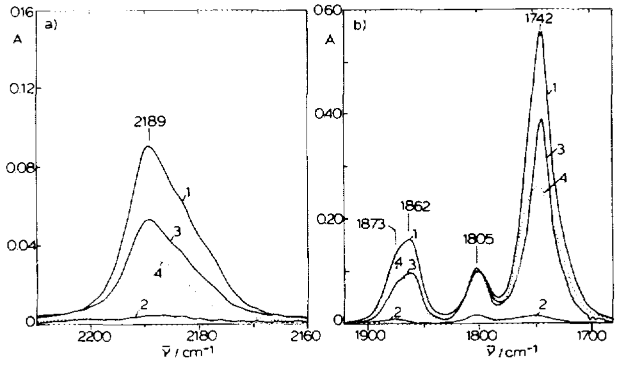


FIG. 3. FT-IR spectra of CO (section a) and NO (section b) adsorbed at RT on the SC0.5 sample. Before adsorption of CO or NO, the sample was first evacuated at 773 K and then submitted to various treatments, as specified hereafter. Curve 1: reduction with CO; curve 2: reduction with H_2; curve 3: reduction with H_2 followed by reduction with CO; curve 4: reduction with H_2 followed by heating in C_3H_8 at 773 K and evacuation at the same temperature for 5 min.

coordinative unsaturation on each chromium. Specifically, $Cr^{II}(A)$, $Cr^{II}(B)$, and $Cr^{II}(C)$ possess three, two, and one coordinative vacancies, respectively. In the s-CO SC0.5 sample, the relative abundance of the three species is 45–52%, $Cr^{II}(A)$; 25–28%, $Cr^{II}(B)$; and 20–30%, $Cr^{II}(C)$. Mainly relying on previous work (13–15, 27), the various bands obtained on CO or NO adsorption on the s-CO reduced catalyst are assigned as follows: 2180 cm^{-1} is the stretching mode of the CO of a monocarbonyl of $Cr^{II}(A)$; 2178 and 2183 cm^{-1} are the symmetrical (sym.) and asymmetrical (asym.) stretching, respectively, of a dicarbonyl of $Cr^{II}(A)$; 2190 cm^{-1} is the CO stretching of a monocarbonyl of $Cr^{II}(B)$; 1855 and 1741 cm^{-1} are the sym. and asym. stretching of a dinitrosyl of $Cr^{II}(A)$; 1870 and 1744 cm^{-1} are the sym. and asym. stretching of a dinitrosyl of $Cr^{II}(B)$; and 1805 cm^{-1} is the NO stretching of a mononitrosyl of $Cr^{II}(C)$.

By comparison with the sample after s-CO treatment, remarkable differences are observed when the oxidised SC0.5 sample is reduced with H_2 at 773 K. A decreased activity is observed toward the formation of both carbonyls (Fig. 1a, spectrum 2) and nitrosyls (Fig. 1b, spectrum 2). It can be noted, however, that the reactivity toward NO is less dramatically affected compared to that toward CO. It is stressed that when H_2 (instead of CO) is used as reducing agent, not only is the intensity of carbonyls and nitrosyls affected, but also the nature of the chromium species involved in their formation is changed. In particular, in the carbonyl region only a broad and weak band at 2185–2187 cm^{-1} is now present, showing no resolved structure (Fig. 1a, spectrum 2). The band arises from an extremely unstable carbonyl species which is in fact completely destroyed after 2 min evacuation at RT. The corresponding spectrum obtained on NO adsorption (Fig. 1b, spectrum 2) consists of two bands at 1873 and 1744 cm^{-1}, whereas bands at 1855 and 1805 cm^{-1} are now absent. All these facts point to the presence of a new chromium species in samples reduced with H_2, which is different from $Cr^{II}(A)$, $Cr^{II}(B)$, or $Cr^{II}(C)$. It is stressed that the broad band at 2185–2187 cm^{-1} cannot disguise the bands of $Cr^{II}(A)$ and $Cr^{II}(B)$ carbonyls. This fact is easily seen by comparing the stability of the carbonyls of $Cr^{II}(A)$ and $Cr^{II}(B)$ species with the stability of the carbonyl present in the s-H_2 sample. Specifically, bands at 2180 and 2190 cm^{-1}, corresponding to the carbonyls of $Cr^{II}(A)$ and $Cr^{II}(B)$, are partially stable on evacuation at RT and can be completely destroyed by evacuation at higher temperature (373 K), whereas the carbonyl present in the s-H_2 sample (broad band at 2185–2187 cm^{-1}) is easily destroyed by evacuation at RT. Moreover, the absence of $Cr^{II}(A)$ and $Cr^{II}(C)$ is shown by the absence of the nitrosyl bands of these two species in the s-H_2 sample.

Based on the findings reported above, it is suggested that Cr^{III} species, hereafter designated as $Cr^{III}(G)$, are formed on the surface of the SC sample reduced with H_2 at 773 K. To substantiate this hypothesis and to gain better insight into the nature of the $Cr^{III}(G)$ species, the following experiments were performed.

In the first experiment, the sample reduced with H_2 at 773 K was subsequently submitted to the s-CO reduction. After this treatment, the spectrum obtained by adsorption of CO at RT (Fig. 1a, spectrum 3) is rather similar to that obtained by adsorption of CO on the s-CO reduced sample, the main difference being a lower intensity (compare spectrum 3 with spectrum 1 in Fig. 1a). The result unambiguously shows the presence in the s-H_2 sample of chromium species which can be further reduced to Cr^{II} by the s-CO treatment (i.e., $Cr^{II}(A)$ and $Cr^{II}(B)$ species can be partially restored). This fact taken together with the finding (from redox cycles) that 0.7 to 1 *e*/Cr are consumed in the reduction with CO of a sample already reduced with H_2 strongly suggests that Cr^{III} is the main species present in the s-H_2 sample.

In a second experiment, after the s-CO reduction, the sample was reacted with H_2O vapour at 623 K, a treatment which is known to oxidise Cr^{II} to Cr^{III} (3, 5, 9). Adsorption of CO (Fig. 1a, spectrum 4) or NO at RT (Fig. 1b, spectrum 4) gives IR spectra nearly identical to those obtained by adsorption of the same gases on the s-H_2 sample. This finding reinforces the conclusion that Cr^{III} is the species present in the s-H_2 sample. The presence of a weak band at 1805 cm^{-1}, arising from $Cr^{II}(C)$ NO, in the sample heated with H_2O at 623 K shows that this temperature is too low to oxidise all Cr^{II} to Cr^{III}.

In another experiment, the s-H_2 reduced sample, after adsorption of NO at RT and therefore showing the dinitrosyl of $Cr^{III}(G)$, was exposed to CO at RT. The absence of significant changes in the spectrum indicates that the $Cr^{III}(G)(NO)_2$ is not prone to adsorb a third ligand at RT, suggesting that $Cr^{III}(G)$ possesses two coordinative vacancies only.

For a better insight into the nature of chromium species present on the surface under reaction conditions, the following experiments were carried out. The results of these experiments are reported in Fig. 2a and 2b, where the spectra obtained by adsorption of CO (spectrum 1, section a of Fig. 2) or NO (spectrum 1, section b of Fig. 2) on the s-CO sample are also reported for a comparison.

The exposure of the s-H_2 reduced sample to propane at 773 K followed by evacuation at 773 K leaves the chromium species present on the surface unaltered after the s-H_2 treatment, as revealed by both CO (compare spectrum 2 of Fig. 2a with spectrum 2 of Fig. 1a) and NO adsorption (spectrum not reported). Hence, the propane, unlike CO, is not capable of reducing Cr^{III} to Cr^{II}.

After the s-CO reduction, when the SC0.5 sample is subsequently heated under vacuum at 773 K, a decreased activity is observed toward both CO (Fig. 2a, spectrum

3) and NO (Fig. 2b, spectrum 3). A transformation of the Cr^{II}(A) into the Cr^{II}(C) species is evidenced by the decrease of the bands at 1855 and 1741 cm^{-1} (dinitrosyl of Cr^{II}(A)), occurring together with the increase of the band at 1805 cm^{-1} (mononitrosyl of Cr^{II}(C)). This transformation has been previously studied (15, 24–27) and interpreted as an activated process causing the transformation of the more protruding Cr^{II}(A) species formed by reduction at low temperature (623 K) into the more shielded Cr^{II}(C). This transformation is practically complete after 3 h in vacuum at 923 K. We have considered here the effect after 30 min at 773 K in vacuum to provide evidence for the different evolution of the chromium species by thermal treatment at 773 K for 30 min in H_2 or in propane.

The results obtained when the s-CO reduced samples are first reacted with H_2 or propane at 773 K and subsequently exposed to CO or NO at RT are now examined. After reaction with H_2 at 773 K, changes with respect to the spectra obtained on the s-CO sample are observed both in the carbonyl (Fig. 2a, spectrum 4) and nitrosyl regions (Fig. 2b, spectrum 4). An inspection of the spectra shows that the concentration of Cr^{II}(A) and Cr^{II}(B) species is much lower compared with that observed in the s-CO sample. No evolution of Cr^{II}(A) and Cr^{II}(B) species toward Cr^{II}(C) is observed. After reaction with propane at 773 K, a surface situation nearly identical to that observed after the treatment with H_2 at 773 K is observed (Fig. 2a and b, spectra 5). Specifically, the concentration of both Cr^{II}(A) and Cr^{II}(B) is substantially lower compared with that observed in the s-CO sample. Also in this case, no evolution of Cr^{II}(A) and Cr^{II}(B) species toward Cr^{II}(C) is observed. We can conclude that both in hydrogen and propane, Cr^{II} species evolve towards a chromium configuration very similar to that present in the s-H_2 sample and in the s-CO sample after heating in water vapour.

The results obtained when analogous adsorption experiments were performed on the SC0.5 sample dehydrated at 773 K are now examined. The corresponding IR spectra observed after adsorption at RT of CO or NO are reported in sections a and b, respectively, of Fig. 3. An inspection of the spectra shows that the species present on the sample evacuated at 773 K are the same as those present in the extensively dehydrated sample (compare spectra 1, 2, and 3 of Fig. 3 with spectra 1, 2, and 3 of Fig. 1). The same IR spectra of carbonyls (section a) and nitrosyls (section b) of Cr^{II}(A), Cr^{II}(B), Cr^{II}(C), and Cr^{III}(G) are also detected in the sample evacuated at 773 K when this sample is subsequently submitted to the same treatments (s-CO, s-H_2, or exposure to propane) as those adopted with the 1023 K evacuated sample. Compared with the 1023 K evacuated sample, the most marked differences in the 773 K evacuated sample are: (i) an overall lower concentration of surface species, particularly carbonyls, (ii) a different relative abundance of the three Cr^{II}species, the Cr^{II}(B) species being the most abundant in the sample evacuated at 773 K, and (iii) the fact that the spectra of carbonyls are much less resolved in the sample evacuated at 773 K. All these features can be accounted for by the higher hydroxyl content in the sample evacuated at 773 K.

The Catalytic Activity of CrO_x/SiO_2, CrO_x/Al_2O_3, and α-Cr_2O_3

The selectivity aspect is considered first. Selectivity to propene is calculated with respect to the sum of C_1 to C_3 hydrocarbons. The sum is always a large fraction (≥95%) of the propane at the inlet of the reactor, but it does not exactly match the propane itself because of the formation of products (coke formation on the surface of the catalyst) which escape the GC analysis. On the whole, the selectivity increases with time on stream from 85 to 98% after 100 min.

During the dehydrogenation reaction at 723 to 823 K, all samples undergo a deactivation process (coke formation), as illustrated in Figs. 4 and 5 for SC catalysts, and in Fig. 6 for AC catalysts. As already mentioned in the Experimental section, rate data are in accordance with the deactivation equation $\ln r = \ln r_0 - \alpha t$, which allows r_0 values to be calculated at $t = 0$. The deactivation is particularly marked on α-Cr_2O_3 at 823 K. With this catalyst, the aforementioned decay equation fits data referring to the early stage of the reaction only. For all samples, the catalytic activity can be entirely restored by means of the s.o. treatment after the slow deactivation occurring during prolonged time on stream.

The influence of the catalyst pretreatment on the rate of propane dehydrogenation can now be considered. This aspect is illustrated for the SC0.5 catalyst in Fig. 4. Before the catalytic activity was tested, the SC0.5 catalyst was in all cases submitted to the s.o. treatment and thereafter *either* exposed directly to the reactant *or* reduced with

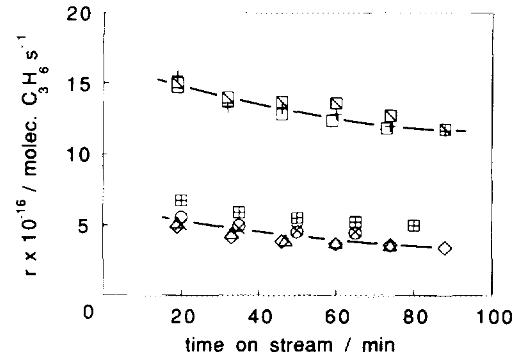


FIG. 4. Dehydrogenation rate vs time on stream on the SC0.5 sample. Reaction at 873 K; (□) sample reduced with CO; (+) reduced with H_2; (⧄) not reduced. Reaction at 773 K: (◇) sample reduced with CO; (△) reduced with H_2. Reaction at 773 K on the sample evacuated at 1023 K: (⊞) reduced with CO at 623 K; (○) reduced with H_2; (×) not reduced.

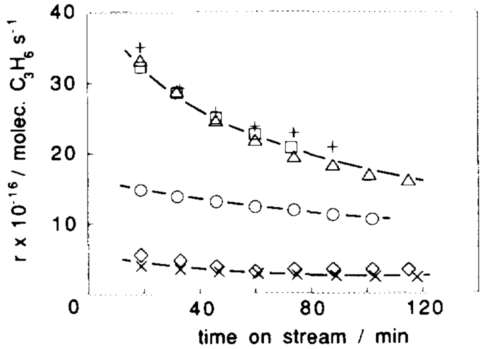


FIG. 5. Dehydrogenation rate vs time on stream on the SC1 sample. Reaction at 823 K: (△) sample not reduced; (□), (+) reduced with H_2 (2nd and 6th cycle). Reaction at 773 K: (○) sample reduced with H_2. Reaction at 723 K: (×) sample reduced with CO; (◇) reduced with H_2.

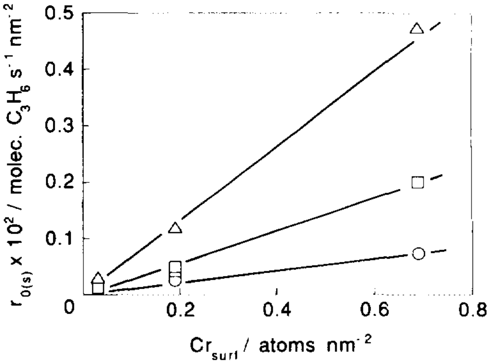


FIG. 7. Dependence of activity on chromium content for CrO_x/SiO_2 catalysts. Specific initial dehydrogenation rate vs surface concentration of chromium. Reaction temperature: (△) 823 K; (□) 773 K; (○) 723 K.

CO or H_2, as specified in Fig. 4. In some cases (specified in the caption to Fig. 4), the SC0.5 sample was dehydrated at 1023 K before the s.o. treatment. At each reaction temperature, the results clearly show that rates are nearly independent of the activation procedure adopted before catalysis. Nearly the same activity is, in fact, measured on samples (i) reduced with CO, or (ii) reduced with H_2, or (iii) directly exposed to propane without prereduction. Also, the dehydration at 1023 K before catalysis has little effect on the catalytic activity (Fig. 4). The absence of an influence of the pretreatment is confirmed on the SC1 catalyst (Fig. 5). Data in Fig. 5 show the good reproducibility and reversibility of SC catalysts after several catalytic experiments (compare experiments 2 and 6 in Fig. 5). Passing to AC catalysts, with this system also no effect of the pretreatment is observed, as shown in Fig. 6 for the catalyst AC0.6 submitted to various pretreatments. Analogously, no effect of the pretreatment is found on α-Cr_2O_3 at 823 K. For example, $r_0 = 2.8 \times 10^{17}$ molecules s^{-1} was measured on α-Cr_2O_3 at 773 K after s.o. and exposure to propane without prereduction, and $r_0 = 3.3 \times 10^{17}$ molecules s^{-1} at the same temperature after s.o. followed by reduction with CO at 623 K.

The influence of heating the catalysts in water vapour was investigated as follows. A portion of the SC0.5 catalyst was activated by s.o. followed by reduction with CO at 623 K. After this treatment, $r_0 = 6.1 \times 10^{16}$ molecules s^{-1} was measured for the dehydrogenation at 773 K. The sample was thereafter submitted to the s.o. treatment, reduced with CO at 623 K, and subsequently heated with H_2O at 773 K. After this treatment $r_0 = 4.4 \times 10^{16}$ molecules s^{-1} was measured at 773 K. In another experiment, identical to the previous one except for the higher temperature (873 K) of the treatment with H_2O, $r_0 = 3.7 \times 10^{16}$ molecules s^{-1} was determined.

As for the dependence of activity on the chromium content, a nearly linear increase of catalytic activity with increasing chromium concentration is observed for both SC and AC catalysts. The results at 723, 773, and 823 K are shown in Fig. 7 and in Fig. 8 for the SC and AC systems, respectively. In the two plots, specific initial rates ($r_{0(s)} = r_0$/S.A., $r_{0(s)}$, molecules s^{-1} m^{-2}) are reported

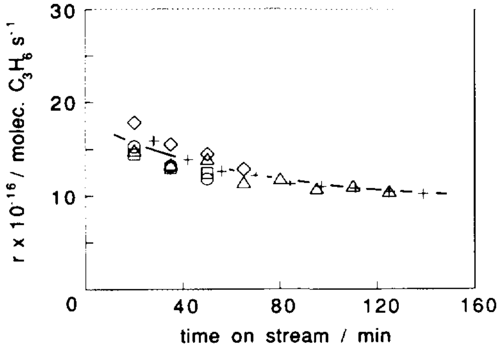


FIG. 6. Dehydrogenation rate at 773 K vs time on stream on the AC0.6 sample. (+,○) not reduced (two different portions from the same batch); (△,◇) reduced with CO (two different portions from the same batch); (□) reduced with H_2; (○) not reduced.

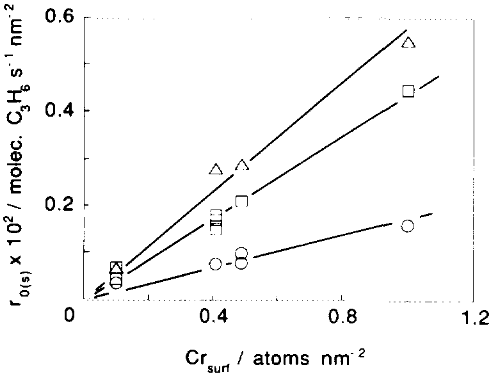


FIG. 8. Dependence of activity on chromium content for CrO_x/Al_2O_3 catalysts. Specific initial dehydrogenation rate vs surface concentration of chromium. Reaction temperature: (△) 823 K; (□) 773 K; (○) 723 K.

TABLE 3

Turnover Frequency (N_{Cr}, molecules s^{-1} $atom^{-1}$) and Apparent Activation Energy (E_a, kJ mol^{-1}) on CrO_x/SiO_2, CrO_x/Al_2O_3, and α-Cr_2O_3 Catalysts

Catalyst	E_a (kJ mol^{-1})	T (K)	$10^3 \times N_{Cr}$ (molec. s^{-1} $atom^{-1}$)
CrO_x/SiO_2	88 ± 10	723	1.1
		773	2.8
		823	6.9
CrO_x/Al_2O_3	67 ± 10	723	1.7
		773	4.3
		823	5.7
α-Cr_2O_3	76 ± 10	723	1.3
		773	2.7
		823	5.6

as a function of the surface concentration of chromium (Cr atoms nm^{-2}). The slope of the various straight lines passing through the origin corresponds to the average turnover frequencies at each temperature. The N_{Cr} values thus calculated are reported in Table 3 for SC and AC catalysts together with those of α-Cr_2O_3. Table 3 also reports the apparent activation energy (E_a, kJ mol^{-1}) for the dehydrogenation of propane on AC, SC, and α-Cr_2O_3 catalysts.

DISCUSSION

The spectroscopic features and the assignment of the IR bands observed on CrO_x/SiO_2 after various treatments having been reported in Results, the Discussion will focus on (i) the nature of the chromium active site and (ii) the role of the support. As regards point (i), oxidation state, coordinative requirements, and nuclearity of the active site will be discussed. The role of the support will be examined by comparing the catalytic activity of CrO_x/SiO_2, CrO_x/Al_2O_3, CrO_x/ZrO_2, and α-Cr_2O_3.

The Nature of the Active Site

In the present investigation, it has been found that the catalytic features (selectivity, initial rates, and decay of activity with time on stream) of SC, AC, and α-Cr_2O_3 samples are not influenced by the reduction procedure (reduction with CO or H_2 or direct exposure to propane) adopted before catalytic experiments. The same behaviour is found with SC, AC, and α-Cr_2O_3 catalysts as observed previously with ZC catalysts (8). A rationalisation for this behaviour was straightforward in the case of ZC catalysts. The characterisation of the ZC system has provided evidence that Cr^{II} and Cr^{III} in nearly equal amounts are formed on the surface of ZC catalysts by reduction with either CO or H_2 (5, 6, 9, 10), and it appeared reasonable to suggest that propane at 773 K was as effective in the sample reduction as CO or H_2 (8). In view of these findings, the same activity is expected on ZC catalysts, irrespective of the reduction mode, given that the same surface composition of chromium species is achieved, irrespective of the activation itself.

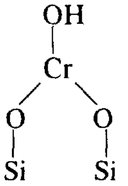
Regarding the SC catalysts, different chromium species are formed on the surface when H_2, instead of CO, is used as reducing agent. In particular, nearly all chromium is in the +2 state after reduction of SC catalysts with CO as shown by IR data reported in the literature (13, 27) and is confirmed here. That all chromium is in the +2 state is also consistent with the average oxidation number of chromium, $\bar{n} = 2$, calculated from the amount of CO consumed during the reduction with CO of SC catalysts. By way of contrast, after reduction of SC catalysts with H_2, (i) only Cr^{III} species are present, and (ii) Cr^{II} species have here been shown to be absent, as evidenced in Results by both IR spectroscopy and data from redox cycles ($\bar{n} = 2.9$).

In view of the marked differences in the surface composition of SC catalysts after the various activation procedures, it is rather surprising that the same activity is observed when SC samples are either reduced with CO or with H_2, or exposed directly to propane at the reaction temperature. The fact that the same activity is found irrespective of the activation mode can be accounted for by considering that under the reaction conditions chromium species in both the s-CO and s-H_2 catalysts evolve towards the same surface configuration, as evidenced by IR experiments. Specifically, upon admission of propane, Cr^{III}(G) is the most abundant surface species in both the s-CO and s-H_2 catalysts. These findings, and particularly the stability of Cr^{III} species contrasted with the instability of Cr^{II} species in the presence of propane, suggest that Cr^{III} species are the active sites for the dehydrogenation of propane and that Cr^{II} does not play any role. Whereas the instability of Cr^{II} species in the presence of propane and/or hydrogen appears well established, the mechanism by which Cr^{II} are transformed into Cr^{III} is not understood at present. A possible role of OH groups from the SiO_2 support to accomplish oxidation of Cr^{II} to Cr^{III} can be suggested. A similar role was invoked by Wittgen *et al.* (28) in an attempt to explain the recovery of activity for the hydrogenation of olefins observed when a CO-reduced SC catalyst (containing Cr^{II}, inactive for the hydrogenation) is subsequently heated in H_2 at 768 K.

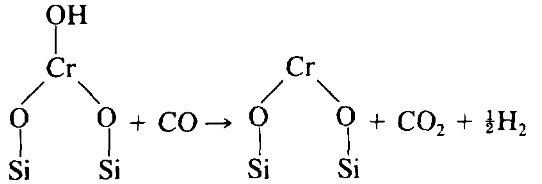
The conclusion that active sites for the dehydrogenation of propane are Cr^{III} rather than Cr^{II} species is further supported by the limited decrease of activity observed when Cr^{II} species (formed by reduction of SC samples with CO) are selectively oxidised with water at 773 K or

873 K. In fact, a much higher decrease of activity would have been detected if Cr^{II} were the active site. The limited decrease observed (a factor 1.6 at most) is easily accounted for by some clumping of Cr^{III} species occurring during the heating with water at high temperature. The occurence of clumping is suggested by IR evidence pointing to a decreased activity of $Cr^{III}(G)$ species toward formation of carbonyls and dinitrosyls when samples heated in water vapour are subsequently exposed to CO or NO at RT. It is recalled that the selective oxidation of Cr^{II} with water vapour at 773 K was also found hardly to affect the activity of ZC catalysts, and on that basis, a role of Cr^{II} for dehydrogenation was ruled out (8).

Considering now the structure of the active site, a model for $Cr^{III}(G)$ can be proposed relying on the following results: (i) the formation of dinitrosyls of the $Cr^{III}(G)$ species upon NO adsorption, (ii) the similarity of IR parameters of $Cr^{III}(G)(NO)_2$ with those of $Cr^{II}(B)(NO)_2$, and (iii) the fact that the dinitrosyls of both $Cr^{III}(G)$ and $Cr^{II}(B)$ are not capable of adding a third ligand at RT. These facts suggest a common nature for $Cr^{III}(G)$ and $Cr^{II}(B)$. Therefore, the following structure is proposed for $Cr^{III}(G)$ analogous to that proposed previously (24–26) for $Cr^{II}(B)$:



The proposed model should be regarded as an example of the possible structures which would conform to the features required by the active site. The model also accounts for the finding that $Cr^{III}(G)$ species, after their formation by reduction with H_2, can be subsequently reduced to Cr^{II} by further reducing the sample with CO at 623 K. The reduction of $Cr^{III}(G)$ to $Cr^{II}(A)$ by CO can be schematically depicted as



As regards the nuclearity of active chromium in SC and AC catalysts, the linear correlation observed between dehydrogenation rates and chromium content (Figs. 7 and 8), and hence the constancy of N_{Cr} in the whole chromium concentration range, suggests mononuclear chromium active sites, as already discussed in the case of ZC catalysts for which the same linear dependence of rates on chromium concentration were observed (8). On the assumption that chromium is randomly distributed on the silica and alumina supports, the constancy of N_{Cr} suggests that special configurations of the active site, such as pairs in Cr–O–Cr arrangements, are unnecessary since an increase of N_{Cr} with chromium concentration would otherwise be expected. However, the presence of pairs or higher polynuclear chromium species should not be detrimental; otherwise a decrease of N_{Cr} at high chromium loading would be expected. A constancy of N_{Cr} for the dehydrogenation of ethane at 768 K on SC catalysts was also observed by Lugo and Lunsford (3) and attributed to low nuclearity chromium active sites.

The Role of the Support

Turnover frequencies for the dehydrogenation of propane at three temperatures on ZC, SC, AC, and α-Cr_2O_3 catalysts are reported in Fig. 9 for a comparison (N_{Cr} values for ZC are taken from Ref. 8). The comparison shows that N_{Cr} values at a given temperature (i) are rather similar for SC, AC, and α-Cr_2O_3, differing by 50% at most, and (ii) are substantially higher (4 to 6 times) for ZC compared to SC, AC, and α-Cr_2O_3 catalysts. The higher activity of ZC catalysts can be explained as follows. Evidence has been previously presented (6, 9, 10) showing that Cr^{III} sites, active for dehydrogenation, arise from reduction of Cr^{V} present in ZC catalysts after the s.o. treatment. The Cr^{V} species are mononuclear (ESR of ^{53}Cr-enriched samples (6, 12) and present at high concentration (50% of total chromium (6, 12) in ZC catalysts. Nearly all Cr^{III} species arising from reduction of Cr^{V} were found to possess two coordinative vacancies, as deduced by taking together IR data showing the formation of $Cr^{III}(NO)_2$ and adsorption data giving NO/Cr ≃ 2 (10). Mononuclear Cr^{V} species are also present on SC and AC catalysts, albeit at a substantially lower concentration. Specifically, on both SC and AC samples Cr^{V} is roughly 10% of total chromium (21). Considering the hypothesis

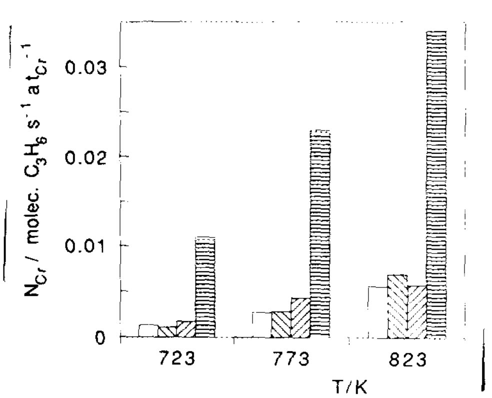


FIG. 9. Turnover frequency for dehydrogenation of propane on α-Cr_2O_3 and on various chromium supported systems at different temperatures: □ α-Cr_2O_3; ▨ CrO_x/SiO_2; ▨ CrO_x/Al_2O_3; and ▤ CrO_x/ZrO_2.

that active Cr^{III} species arise from reduction of Cr^{V} in SC and AC samples as well, roughly 5 times higher N_{Cr} values are expected in the case of ZC catalysts. This is in fair agreement with N_{Cr} values measured on ZC which are 4 to 6 times higher compared with SC and AC catalysts.

An important role of the support emerges. This role is manifold: (i) to control the Cr^{V} concentration and that of the related Cr^{III} species obtained on reduction, (ii) to stabilise Cr^{III} after reduction and/or in the presence of the reactant mixture, and (iii) to provide surface sites in which the proper coordination of chromium is preserved (two coordinative vacancies on Cr^{III}). Another important role of the support is to enter directly into the structure of the active site through the oxygen ions bonded to both chromium and support cations. One argument in favour of participation of the oxygen ions of the support has been given in a previous paper discussing the negative effect of potassium addition on the catalytic activity of ZC samples (8). The role played by oxygen anions is not assessed; these species, however, might be involved in the dissociative adsorption of propane as well as in the hydrogen desorption step.

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