

Oxygen adsorption and catalytic performance in oxidative dehydrogenation of isobutane on chromium oxide-based catalysts

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Received 4th August 1998, Accepted 25th November 1998

Oxygen adsorption on γ -Al₂O₃-, TiO₂ (anatase)-supported chromium oxide and on unsupported chromia in amorphous and crystalline form, has been studied with a gravimetric method in the temperature range 523–623 K. The equilibrium oxygen uptake at $p \rightarrow \infty$ was the same for all the studied catalysts, the rate of the adsorption was, however, different, increasing in the order: CrO_x/Al₂O₃ < CrO_x/TiO₂ < Cr₂O₃ amorph. < Cr₂O₃ cryst. Measurements of oxidative dehydrogenation of isobutane on the catalysts given above have shown that the selectivity to isobutene decreases in the same sequence. The higher selectivity values and the change in the rate constant of the isobutane oxidative dehydrogenation with conversion, observed for the Al₂O₃- and TiO₂-supported chromium oxide catalysts, have been ascribed to the lower coverage of the surface of the catalyst with oxygen in the stationary state of the isobutane oxidative dehydrogenation, as compared with unsupported chromia.

1 Introduction

Supported chromium oxide systems have been known, for many decades, as active catalysts in a number of hydrocarbon reactions such as polymerization,¹ and dehydrogenation and dehydrocyclization,^{2–6} and have been studied also in the selective reduction of nitrogen oxides in the presence of oxygen.^{7–9}

Quite recently, we have found that supported chromium oxides are active and selective in oxidative dehydrogenation (OHD) of isobutane.^{10–12} The product of this reaction, isobutene, is a key reactant for the production of methyl *tert*-butyl ether (an additive for lead-free petrol), and of acrylic acid and methacrylates. The best results in the ODH of isobutane have been obtained with CrO_x/Al₂O₃ and CrO_x/TiO₂ systems, which are active at relatively low temperatures 473–523 K.^{10–12}

Both the selective reduction of nitrogen oxides and the ODH of isobutane involve adsorption of oxygen and reoxidation of the catalyst surface as the reaction steps. Studies of the interaction of oxygen with the catalyst are, hence, essential to obtain an explanation of the mechanism of the catalyst action and of the reaction mechanism on a molecular scale.

Adsorption of oxygen on pure chromia has been studied since the 30s, initially at low temperatures.^{13–16} The results of the early studies on this subject can be found in a monograph by Trapnell.¹⁷ Winter¹⁸ included Cr₂O₃ in his extensive studies on isotopic exchanges of oxygen on oxides. The low-temperature oxygen adsorption on supported chromia has been proposed as a method for the determination of the area of chromia on a support.¹⁶ High-temperature adsorption of oxygen on pure and alumina-supported chromia, studied by Voltz and Weller¹⁹ and Dereń and Haber,^{20,21} has been related to the oxidation of the surface Cr³⁺ ions to Cr⁶⁺.

Oxygen chemisorption on chromia and supported chromia systems has been found to be dissociative, even at room temperature, as indicated by the high adsorption heat. Monoatomic oxygen species are present in different surface Cr=O

groups, in which oxygen is bound with different strengths. As shown in the IR studies of Zecchina *et al.*,²² the Cr=O stretching frequency (an indicator of the Cr–O bond energy) for Cr₂O₃ depends both on the coordination number of the adsorbing chromium ions and on the environment of the Cr=O groups: several different chromyl groups have been identified on the surface of chromia in these studies. In recent years, the presence of different oxygen species deriving from different types of chromium–oxygen complexes on the surface of chromia and supported chromia systems, has been postulated from studies with hydrogen temperature-programmed reduction (TPR),^{11,23–27} X-ray photoelectron spectroscopy (XPS),^{27–31} EPR^{32–34} and Raman and IR^{22,31,35–38} spectroscopies. Isolated and polymerized CrO_x polyhedra containing Cr³⁺, Cr⁵⁺, and Cr⁶⁺ ions have been identified on the surface of oxide supports, in addition to exposed Cr³⁺ ions of different degree of coordinative unsaturation. The latter species are mainly observed on the surface of pure Cr₂O₃. The presence and distribution of different [CrO_x]_n species on the supports depend on the nature of the support, the chromium loading and the preparation conditions. At higher Cr content, amorphous and crystalline α -Cr₂O₃ are also observed in the chromium oxide/support systems.

Both low- and high-temperature adsorption of oxygen on supported systems have been studied, mostly to determine the area of the chromia phase on the support. Only in a few cases have correlations been sought between the data on oxygen chemisorption and the catalytic performance of chromia-containing systems *e.g.* in the oxidation of CO to CO₂,¹⁶ or in polymerization.³⁹

In the present work, oxygen chemisorption has been studied on selected CrO_x/Al₂O₃ and CrO_x/TiO₂ catalysts which have shown the highest activity and selectivity to isobutene in the ODH of isobutane,^{11,12} and an attempt has been made to correlate the data on oxygen adsorption with the catalytic performance for this reaction. For comparison, the chemisorption of oxygen and isobutane ODH on unsupported chromia, both in amorphous and crystalline forms have also been examined.

Since the ODH of isobutane is the first selective oxidation-type reaction of hydrocarbons reported on chromium oxide-based catalysts, it seemed of interest to check to what extent the general principles of selective oxidation are fulfilled in catalysts of this type. Oxygen adsorption has been studied in conditions close to those used in the catalytic reaction of the ODH of isobutane; particular interest has been paid to measurements of the kinetics of the oxygen sorption, which may determine the oxidation state of the surface during the catalytic oxidation reaction. Additionally, the state of the catalyst surface has been checked by measurements of surface potential (work function) performed *in situ*, in the reaction mixture. It has been shown previously^{40,41} that this technique can provide some qualitative information about the reduction of the catalyst during reactions on oxide catalysts.

2 Experimental

Catalysts

The supported catalysts $\text{CrO}_x/\text{Al}_2\text{O}_3$ and $\text{CrO}_x/\text{TiO}_2$ were prepared as described previously.^{11,12} They were obtained by impregnation with an aqueous solution of chromium nitrate (p.a., POCH, Poland) of the Al_2O_3 support (γ -phase, basic Merck, $111 \text{ m}^2 \text{ g}^{-1}$, 60–200 μm), and the TiO_2 (anatase, Police, Poland, $8 \text{ m}^2 \text{ g}^{-1}$) followed by drying for 5 h at 393 K and calcination in a flow of air at 773 K.

The Cr content corresponded to *ca.* one theoretical monolayer of Cr_2O_3 on the support surface. One monolayer of Cr_2O_3 , was estimated from the crystallographic data of the oxide as equivalent to 10 atoms of Cr per 1 nm^2 of the support, in agreement with MacIver and Tobin.¹⁵ The samples are denoted further in the text by symbols 10 CrAl (Ti).

No crystalline Cr_2O_3 was observed in the samples on XRD examination, the Raman spectroscopy revealed, however, a sharp band at *ca.* 560 cm^{-1} , characteristic of Cr_2O_3 , in addition to intense bands in the region $8000\text{--}1000 \text{ cm}^{-1}$ ascribed to the presence of polychromates for the 10 CrAl samples.¹¹ The Raman spectra of the 10 CrTi sample did not show the bands characteristic of the Cr–O vibrations, owing to the low amount of the deposited chromium phase. The bands corresponding to the polychromates were observed, however, when TiO_2 of higher specific surface area (and thus of higher amount of chromium oxide phase at 1 monolayer content) was used. Both samples contained chromium ions in an oxidation state higher than $3+$, as revealed by chemical analysis with the Bunsen–Rupp (BR) method and the XPS technique.^{11,12} The BR method consists in treating a sample with concentrated HCl at 373 K for 30 min and determining the chlorine evolved by iodometric titration.⁴² In the case of the 10 CrAl sample, the total excess charge determined by this method was attributed to Cr^{6+} ions only,¹¹ in the case of the 10 CrTi sample Cr^{5+} ions were also detected by XPS and EPR.¹² For both samples, the results of the BR analysis were, however, expressed in terms of a number of Cr^{6+} ions per nm^2 of catalyst surface.

Amorphous Cr_2O_3 was prepared following the method described by Curry-Hyde and Baiker,²⁴ by slow precipitation from chromium nitrate with ammonia, drying and treatment at 623 K for 3 h in a stream of hydrogen, followed by calcination at 573 K in air for 3 h. Crystalline Cr_2O_3 was obtained by calcination of the amorphous chromia in air at 873 K for 6 h. XRD analysis of the chromium oxides thus obtained showed a pattern characteristic of $\alpha\text{-Cr}_2\text{O}_3$, in accordance with the ASTM data, no diffraction lines were observed for the first (amorphous) sample.

Table 1 gives the basic characteristics of the studied samples, including specific surface area (determined by the

Table 1 Basic characteristics of chromium catalysts

Catalyst	Cr_{tot} (wt.%)	Specific surface area $/\text{m}^2 \text{ g}^{-1}$	$\text{Cr}^{6+}/\text{atom nm}^{-2}$		
			Fresh catalyst		After reaction ^c
			BR ^a	TPR ^b	BR ^a
10 CrAl	8.4	104	2.64	2.43	0.06
			1.98	—	—
10 CrTi	0.6	8	4.30	—	—
$\alpha\text{-Cr}_2\text{O}_3$	68.4	28	3.93	3.56	0.71
amorph. Cr_2O_3	68.4	210	6.34	—	—

^a Determined by the Bunsen–Rupp method. ^b Determined by the TPR method (ref. 11). ^c Catalysts, *ex situ*, after ODH of IB at 523 K for 10 h, then cooled down in the reaction mixture. ^d After evacuation at 1×10^{-4} kPa and 623 K for 24 h.

BET method with argon as an adsorbate), and the content of Cr ions of valency higher than $+3$, both for fresh samples and after ODH of isobutane.

The results indicate that, beside Cr^{3+} ions, the surface of the catalysts contains a considerable fraction of oxidized chromium ions.

Chemisorption of oxygen

This was studied by a gravimetric method using a S 3DV Sartorius microbalance coupled to a conventional vacuum system. 0.5 g of sample was degassed at 623–648 K at a pressure below 1×10^{-4} kPa for 24 h till a constant mass was obtained and then cooled down to the measurement temperature. Oxygen (99.0%), purified by vacuum distillation, was then introduced and the mass gain was recorded until constant mass was attained. The measurements were carried out in the temperature range 573–648 K and the oxygen pressure range 0.5–15 kPa. In view of the large volume of the experimental set-up the measurements were carried out in isobaric conditions. The accuracy of the measurement was $1 \mu\text{g}$. It was checked, in preliminary experiments, that the oxygen uptake was reversible in successive degassing–adsorption cycles. The control chemical analysis of the 10 CrAl sample after degassing in vacuum and cooling to room temperature showed a decrease in the total Cr^{6+} content with respect to the fresh sample of *ca.* 30%. The initial value of the Cr^{6+} content was, however, restored after the oxygen chemisorption measurements. These facts suggest that the oxygen uptake consists of reoxidation of the Cr^{3+} ions, reduced by vacuum pretreatment, to Cr^{6+} .

The rate of adsorption was obtained from the slope of a curve of the mass gain *vs.* the adsorption time. For small time intervals:

$$r_a = \frac{1}{16m_o S} \frac{\Delta m}{\Delta t} \quad [(\mu\text{mol O}) \text{ s}^{-1} \text{ m}^{-2}] \quad (1)$$

where Δm is the mass gain of the sample (μg) in the time interval Δt (s), m_o the sample mass (g), S the specific surface area of the sample ($\text{m}^2 \text{ g}^{-1}$).

In analysis of the adsorption kinetics the adsorption rate related to the coverage of the surface with oxygen was used:

$$R_a = \frac{d\theta}{dt} \quad (\text{s}^{-1}) \quad (2)$$

where $\theta = \Delta m/(\Delta m)_\infty$, and $(\Delta m)_\infty$ is a mass gain corresponding to equilibrium adsorption at a given temperature (a limiting value of Δm at time $\rightarrow \infty$ and at $p \rightarrow \infty$).

In order to obtain the maximum coverage with adsorbed oxygen, adsorption isotherms were determined at 623 K in the pressure range 0.2–15 kPa. Measurements at pressures lower than 0.2 kPa were not possible owing to the thermomolecular

effects (thermal transpiration) in the vacuum microbalance system, which caused apparent changes of the sample mass.

Surface potential

Surface potential Φ , was measured by the vibrating condenser method; the method and the experimental set-up have been described in ref. 43. The measurements were performed under a flow of 20% O_2 in Ar in the temperature range 323–723 K, and in the flow of reaction mixture: isobutane (IB)– O_2 –Ar = 9.2/18.2/72.6 vol.% in the temperature range 523–603 K. The total flow rate was 300 ml min^{-1} . At each temperature the samples were kept in a flow of O_2 –Ar, or IB– O_2 –Ar mixture for 3–5 h till a constant value of Φ was obtained. The measurements were performed with increasing and decreasing temperature: no change in the Φ values was observed within the limits of the experimental error (± 5 mV). The values of the surface potential are given relative to the graphite electrode, an increase in Φ indicating that the surface becomes more negatively charged.

Catalytic activity measurements

The activity of the catalysts in the ODH of IB was measured in a fixed-bed flow apparatus at 523 K. A stainless-steel reactor (120 mm long, id 13 mm) was coupled directly to a series of gas chromatographs. Isobutene, CO_2 and CO were found to be the main reaction products. The amounts of the degradation products (C_2 , C_3) and of oxygenates (methacrolein and methacrylic acids) were <1% of the total amounts of products. The carbon balance calculated taking into account isobutene, CO and CO_2 was $97 \pm 2\%$ for conversion of IB $\geq 10\%$, at lower conversion the C balance was poorer ($90 \pm 5\%$). The reaction mixture contained 9.2 vol.% IB (Phillips Petroleum Corp., 99%) in air. 0.5 ml catalyst sample (grain size 0.63–1 mm) diluted (1 : 1) with glass beads of the same diameter were used. It was checked in preliminary measurements in which the mass and the grain size of a sample were varied, that, under these conditions, transport phenomena do not limit the reaction rate. For each sample the measurements were performed at contact times varying between 0.1 and 4 s which were obtained by changing the flow rate of the reaction mixture. The total conversion of IB did not exceed 20%.

The catalytic data are presented in the form of plots of selectivities to different products S_p vs. the total conversion of IB, conversion = $(C_i - C_f)/C_i \times 100$, $S_p = C_p/\Sigma C_p$, where C_i and C_f are the concentrations of IB at the entrance and the exit of the reactor, respectively, and C_p is the concentration of product p in exit gas. For a given sample the values of the conversion and S were reproducible within 2–5%. The total rates of IB disappearance per unit of the catalyst surface, r_{sp} , were also calculated for different values of the total conversion.

A blank test without a catalyst or with glass beads in the reactor showed no conversion of IB at the reaction temperature. Pure alumina support was not active either, the IB conversion at 523 K being <0.05%. No deactivation of the catalysts was observed during 10 h of measurement.

Table 2 Oxygen adsorption data for chromia catalysts

Catalysts	Temperature /K	a_∞^a (atom O) nm^{-2}	$\ln k_a^o$	E_a^o / $kJ mol^{-1}$	α / $kJ mol^{-1}$
10 CrAl	573–648	1.10	34.5	213 ± 10	32.4
10 CrTi	523–623	1.23	1.53	44 ± 5	34.3
α - Cr_2O_3	523–623	1.25	9.98	54 ± 5	32.4
amorph. Cr_2O_3	524–573	1.29	13.3	98 ± 10	23.5

^a Maximum adsorption at 573 K.

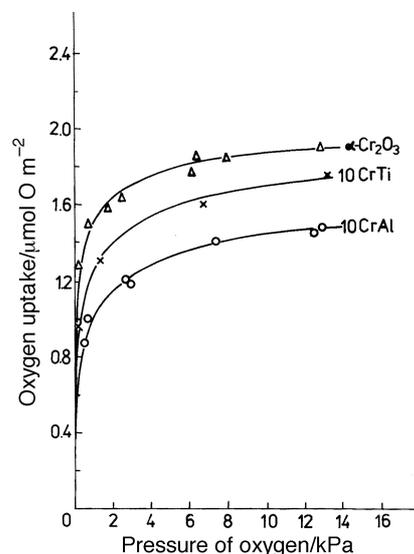


Fig. 1 Isotherms of oxygen adsorption on α - Cr_2O_3 , 10 CrTi and 10 CrAl catalysts at 623 K.

3 Results and discussion

Oxygen chemisorption

Fig. 1 shows typical isotherms of oxygen adsorption at 623 K for 10 CrAl, 10 CrTi and α - Cr_2O_3 catalysts. The experimental data can be described by the Langmuir isotherm for the dissociative adsorption (the correlation coefficient = 0.999):

$$\Theta = \frac{\Delta m}{(\Delta m)_\infty} = \frac{b p_{O_2}^{0.5}}{1 + b p_{O_2}^{0.5}} \quad (3)$$

where b is an adsorption coefficient and P_{O_2} the oxygen pressure.

The lines given in Fig. 1 correspond to the values calculated from eqn. (3). The values of maximum adsorption (a_∞) corresponding to $(\Delta m)_\infty$ for different catalysts are summarized in Table 2. They do not differ much and are equivalent to 7.5–8.5% of an oxygen monolayer, corresponding to the closest hexagonal oxygen packing of oxygen ions in oxides (14.7 at $O nm^{-2}$).

For all the catalysts studied the rate of oxygen uptake (oxygen adsorption) was determined as a function of oxygen pressure, temperature and degree of coverage of the surface. As shown in Fig. 2 the initial rate of the oxygen adsorption (at $\Theta = 0$) is proportional to $p_{O_2}^{0.5}$, which suggests the dissociative character of the O_2 adsorption. At constant oxygen pressure, the adsorption rate decreases rapidly with the increase in the oxygen coverage. Kinetics of this process can be described by

$$R_a = k_a p_{O_2}^{0.5} (1 - \Theta) e^{-\alpha \Theta} \quad (4)$$

where k_a is the adsorption rate constant and α is a constant.

Eqn. (4) is a generalized form of the Elovich equation.⁴⁴ According to Elovich, Roginski and Zeldovich⁴⁵ the exponential term in the equation indicates the energetic inhomogeneity of the surface, the activation energy of the adsorption process

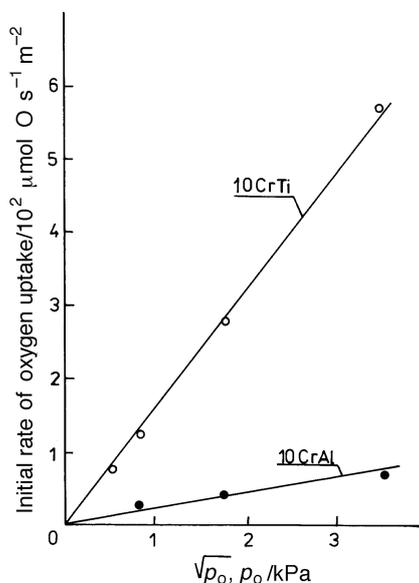


Fig. 2 Initial rate of adsorption of oxygen as a function of the square root of the oxygen pressure, $p_{\text{O}}^{0.5}$, for 10 CrAl and 10 CrTi catalysts.

increasing linearly with increase in θ :

$$E = E_0 + \alpha\theta \quad (5)$$

The constant α characterizes the degree of the energetic inhomogeneity of the surface, high values of α corresponding to a high degree of inhomogeneity. The inhomogeneity of sites on chromia supported on alumina has been previously reported for nitric oxide adsorption on this system.⁴⁶ Eqn. (4) can be easily transformed to a linear form:

$$\ln[RP_{\text{O}}^{-0.5}(1-\theta)^{-2}] = \ln k_a - \alpha\theta \quad (6)$$

Fig. 3 presents kinetic data at 623 K for the studied samples plotted in coordinates of eqn. (6). Analogous curves have been found for lower adsorption temperatures. The values of E_a° , $\ln k_a^\circ$ and α for the studied catalysts are reported in Table 2. The values of the initial activation energy, E_0 , and the pre-exponential factor $\ln k_a^\circ$ at $\theta = 0$ for the process of oxygen chemisorption differ considerably. A compensation effect can, however, be observed, the high values of E_0 corresponding to a high pre-exponential factor: the low values of E_0 are, on the other hand, accompanied by low values of $\ln k_a^\circ$.

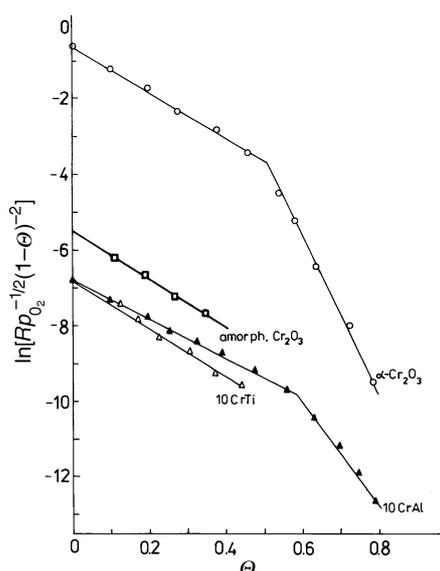


Fig. 3 Rate of oxygen adsorption at 623 K as a function of oxygen coverage, θ , in coordinates of eqn. (6).

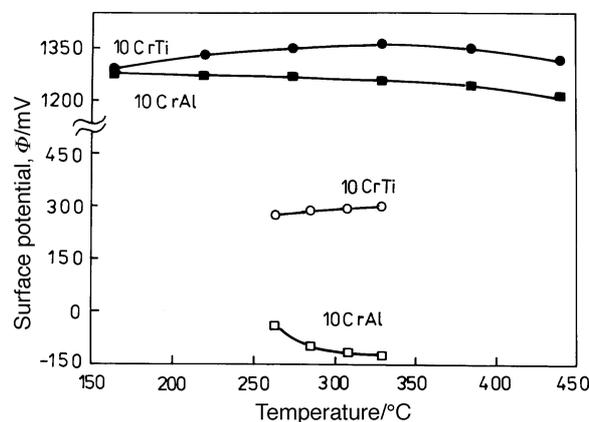


Fig. 4 Surface potential values for 10 CrTi and 10 CrAl catalysts at different temperatures. Filled symbols: in O_2 -Ar atmosphere, open symbols: in IB-O_2 -Ar mixture.

Coefficient α does not vary markedly for the studied catalysts, indicating that the extent of the surface inhomogeneity is similar in all the samples.

Surface potential

Fig. 4 shows the changes in the surface potential, Φ , with temperature for the 10 CrAl and 10 CrTi catalysts in an oxygen atmosphere and in a flow of the IB-O_2 -Ar reaction mixture. For both samples, the Φ values in oxygen are high and do not vary much with temperature. The 10 CrTi catalyst shows slightly higher values (by ca. 0.1 V) as compared with the 10 CrAl sample. The Φ values in the IB-O_2 -Ar reaction mixture are considerably lower (by 1–1.5 V) than those in oxygen, and are significantly higher (by 0.3–0.5 V) for the 10 CrTi sample as compared with the 10 CrAl one. The lower Φ values in the reaction mixture, as compared with those in oxygen, indicate the lower negative charge of the surface. The lowering of the Φ values in the hydrocarbon–oxygen reaction mixture has been observed previously for vanadia titania catalysts⁴¹ and was ascribed to the impoverishment of the surface in negatively charged oxygen species: O^{2-} , or O^- *i.e.* to partial reduction of the catalyst surface. The present results suggest, then, that the surface of both CrAl and CrTi catalysts is partially reduced in the stationary state of the catalytic reaction, the CrAl sample being more reduced than the CrTi catalyst. The Φ values for the CrTi catalyst hardly change with the temperature, whereas those for the 10 CrAl decrease slightly between 523 and 573 K and remain constant at higher temperatures. This suggests that, for the latter catalyst, the surface is less oxidized at the higher reaction temperatures.

Catalytic activity

Fig. 5 shows the dependence of the total conversion of isobutane on the contact time, and Fig. 6 and 7 give the selectivities to isobutene, CO_2 and CO as a function of IB conversion, for all the catalysts under study. As seen, for all the catalysts, the selectivity to isobutene decreases with the increase in IB conversion (increasing contact time). This implies a sequential reaction pathway in which isobutene formed in the first step is further oxidized to CO_2 . Extrapolation to zero conversion indicates, moreover, that a fraction of CO_2 is formed by a parallel route. The selectivity to CO (a minor product) increases with isobutene conversion for the 10 CrAl, 10 CrTi and amorphous Cr_2O_3 , and does not change with conversion for crystalline α - Cr_2O_3 . Moreover, as indicated by the data extrapolated to zero conversion, CO is formed in a parallel reaction on chromium oxides, both in amorphous and crystalline form, whereas for 10 CrAl and 10 CrTi it is produced only by the consecutive path.

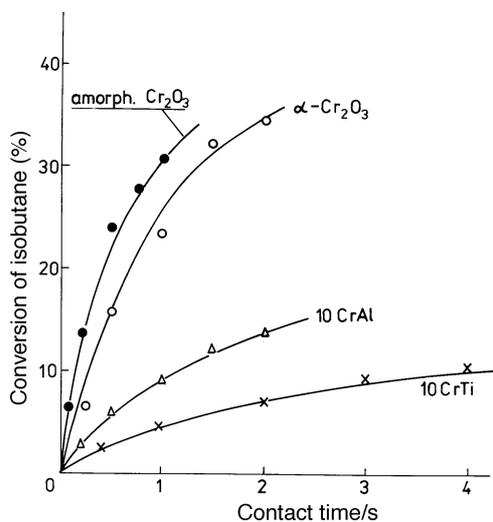


Fig. 5 Total conversion of IB as a function of contact time for unsupported chromia and for 10 CrAl and 10 CrTi catalysts at 523 K.

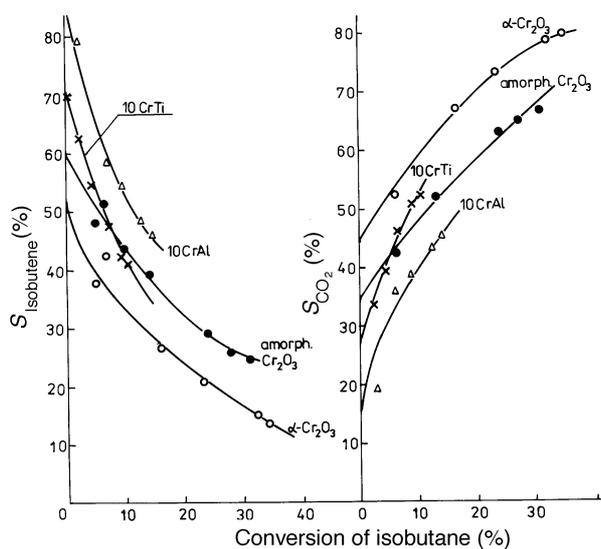


Fig. 6 Selectivities to isobutene and CO_2 as a function of the total IB conversion for unsupported chromia and for 10 CrAl and 10 CrTi catalysts. Reaction temperature, 523 K.

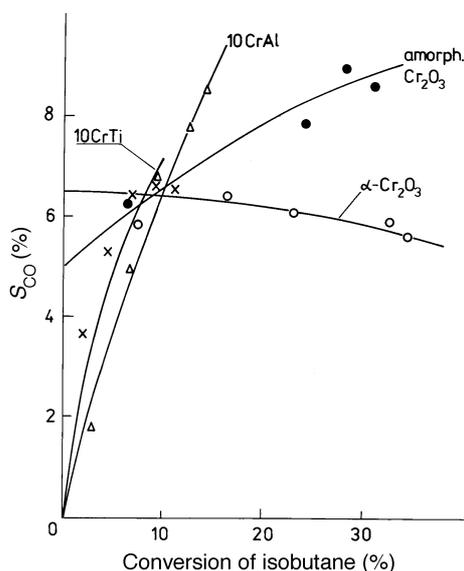
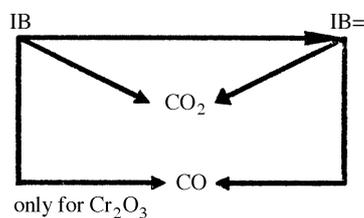


Fig. 7 Selectivity to CO as a function of the total IB conversion for unsupported chromia and for 10 CrAl and 10 CrTi catalysts. Reaction temperature, 523 K.

The mechanism of the isobutane ODH on the studied catalysts can then be described by the following parallel-consecutive scheme:



where IB and IB= stand for isobutane and isobutene, respectively.

It can be mentioned that the parallel-consecutive mechanism is typical for selective oxidation of hydrocarbons leading to the formation of oxygenated products⁴⁷ and has also been found for the ODH of propane on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.⁴⁸

As seen from Fig. 6, the selectivities to isobutene at comparable conversions are different for different catalysts, decreasing in the order: 10 CrAl > 10 CrTi > amorph. Cr_2O_3 > α - Cr_2O_3 . The selectivities to CO_2 increase in the same sequence. No distinct correlation is found between the nature of the catalyst and the selectivity to CO: it can, however, be observed that the selectivities to this product are rather low and the error in the determination of the CO content may be high, which does not permit detailed discussion on the CO formation.

To compare the activity of the studied catalysts, the specific rate of IB disappearance referred to the unit of specific surface area, r_{sp} at different degrees of conversion, has been calculated by numerical differentiation of the conversion-contact time curves. The measurements of r_{sp} at different partial pressures of IB, C_{IB} and oxygen C_O have shown that the reaction order with respect to IB is 1, whereas that with respect to oxygen is 0.5, i.e.

$$r_{sp} = k_r C_{IB} C_O^{0.5} \quad (7)$$

Fig. 8 presents the plot of the $r_{sp}/C_{IB} C_O^{0.5}$ ratio, (corresponding to the rate constant k_r) vs. the total conversion of IB for the studied catalysts. The horizontal straight lines observed for amorphous and crystalline Cr_2O_3 indicate that for these samples eqn. (7) is valid, i.e. k_r is constant over a wide conversion range. For the 10 CrAl and 10 CrTi catalysts, the rate constant decreases with conversion, the effect being particularly pronounced for the latter catalyst. Such behaviour may be ascribed to a decrease in the number of active centres

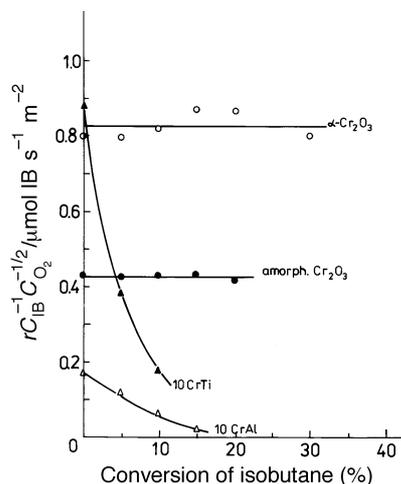


Fig. 8 Rate constant for the disappearance of IB in the ODH reaction, as a function of the total IB conversion for unsupported chromia and 10 CrAl as 10 CrTi catalysts. Reaction temperature, 523 K.

(the pre-exponential factor in the Arrhenius equation) when the total conversion increases, and/or to the change in the reaction mechanism (*e.g.*, the change in the rate-determining step), which could give rise to different activation energies for the reaction.

4 Discussion

A tentative explanation of the properties of the studied catalysts in the ODH of IB can be proposed by comparing the catalytic data with those obtained in the oxygen adsorption studies, supplemented by chemical analysis and surface potential measurements. Let us observe, in the first place, that preliminary studies with the pulse method of the ODH of IB on Cr_2O_3 and 10 CrAl catalysts have shown practically the same initial activity and selectivity in the presence and absence of gaseous oxygen.⁴⁹ This suggests that the redox, Mars and Van Krevelen mechanism,⁵⁰ common for most of the selective oxidation reactions,⁴⁷ operates also in the case of IB ODH on chromia-based catalysts. According to this mechanism, the oxidation reaction proceeds in two steps: (a) reduction of an oxidized catalyst by a hydrocarbon molecule, with incorporation of the catalyst oxygen into the oxidation products (water in the case of the ODH reactions), and (b) reoxidation of the reduced catalyst involving dissociative adsorption of the gaseous oxygen present in the reaction mixture and the electron transfer. It is logical to assume that, in the chromia-based catalysts, the centres for step (a) involve Cr^{6+}O_x groups, present in the studied catalysts as indicated by chemical analysis, XPS and Raman spectroscopy,^{11,12} whereas exposed Cr^{3+} ions provide centres for the catalyst reoxidation (the oxygen uptake). The surface potential measurements and the chemical analysis indicate that the catalysts are partially reduced during the catalytic reaction *i.e.* both Cr^{6+} and Cr^{3+} species do exist on the surface. It follows, from the Mars and Van Krevelen mechanism, that the coverage of the catalyst surface with oxygen in the stationary state of the oxidation reaction depends on the relative rates of the catalyst reduction and reoxidation. The higher rates of oxygen chemisorption observed for unsupported Cr_2O_3 , both amorphous and crystalline, as compared with those for 10 CrAl and 10 CrTi catalysts, suggest higher coverage with oxygen during the IB ODH reaction in the case of Cr_2O_3 . This is indeed confirmed by the results of chemical analysis, which show a higher content of hexavalent Cr species equivalent to surface oxygen after the IB reaction for unsupported chromia, as compared with the 10 CrAl catalyst. Higher coverage with oxygen implies that the number of oxygen atoms in the vicinity of the reacting hydrocarbon molecule is higher, which could account for the higher selectivity to CO_2 observed for unsupported chromia. It has been recognized that one of the prerequisites for a selective oxidation catalyst is a limited number of active oxygen species surrounding an adsorbed hydrocarbon molecule: if this number is high, the molecule, subjected to simultaneous attack of several oxygens at different carbon atoms, undergoes total oxidation to carbon oxides.⁵¹

The lower reoxidation rate of the supported chromium oxide catalysts as compared with pure chromia may be due to the lower surface concentration of the Cr^{3+} centres on which adsorption of the oxygen molecule takes place. TPR, TPD and allyl iodide probe reaction measurements^{11,12} have shown that the $\text{Cr}^{6+}-\text{O}$ bond energy is higher for the supported samples than for unsupported chromia, most probably due to the presence of $\text{Cr}^{6+}-\text{O}-\text{Al}$ and $\text{Cr}^{6+}-\text{O}-\text{Ti}$ bonds in the supported catalysts, stronger than those in $\text{Cr}^{6+}-\text{O}-\text{Cr}^{6+}$ groups on the surface of Cr_2O_3 .

The vacuum pretreatment prior to the chemisorption measurements will, then, lead to more extensive reduction of the $\text{Cr}^{6+}-\text{O}$ groups, with formation of higher amounts of the oxygen adsorption active centres, Cr^{3+} in the case of un-

ported Cr_2O_3 . Moreover, the dissociation of the oxygen molecule requires the presence of the two reduced centres in close vicinity:⁵² this condition should be more easily fulfilled in the case of pure chromia, which is reduced to a greater extent, than for that dispersed on the support CrO_x groups, reduced to a lesser extent. Another factor, which may affect the reoxidation rate, is the ease of electron transfer accompanying the passage from an oxygen molecule to an O^2 species, which requires four electrons.

One may speculate that electron transfer should be easy on the chromia surface, occurring along the $\text{Cr}^{3+}-\text{O}-\text{Cr}^{6+}-\text{O}-\text{Cr}^{3+}-\text{O}$ chains. When the CrO_x units are isolated on the support surface electrons can be transferred to the oxygen molecule from only a limited number of Cr ions. Such an effect could account for the high activation energy of the oxygen chemisorption (reoxidation) observed for the CrAl catalysts, which leads to the low rate of reoxidation. In the case of the CrTi catalysts, for which the value of the activation energy has been found to be much lower, electron transfer could be easier, since the reducible ions, Ti^{4+} , of the support may participate in the exchange of electrons between the distant Cr^{3+} ions. The low rate of oxygen chemisorption for this catalyst is due to the low value of the pre-exponential factor k_0 for which no explanation can be given at present.

The difference in the oxygen adsorption rates may also account for the different course of the rate constant *vs.* conversion curves observed for unsupported Cr_2O_3 and for 10 CrAl and 10 CrTi catalysts. It can be suggested that, for unsupported chromia, the high rate of catalyst reoxidation ensures constant, high coverage of the surface with oxidized species, even at high conversions. The reaction rate may then be determined by the rate of reduction of the catalyst with IB [step (a)]. For the 10 CrAl and 10 CrTi catalysts, with increase in conversion the surface becomes more and more reduced, as the relatively slow reoxidation step cannot keep pace with the enhanced reducibility of the surface [both the primary IB reaction and consecutive isobutene transformations to CO_2 participate at higher conversions in the reduction step (a)]. The reaction rate would then fall as a result of the smaller number of active Cr^{6+}O_x species. On the other hand, at higher conversions, catalyst reoxidation [step (b)] may become the rate-determining step, which could also lead to a decrease in the total activity.

Detailed kinetic studies of IB ODH, now in progress, are necessary to distinguish between these two ways of accounting for the fall in activity with IB conversion, observed for 10 CrAl and CrTi catalysts.

Acknowledgements

The assistance of Mrs. K. Samson, M. Eng. and T. Bobińska, M. Eng. in the preparation and chemical analysis of the catalysts, Mrs. Z. Czula in the BET determinations, and Mrs. I. Gressel in the technical preparation of the typescript is gratefully acknowledged. The surface potential measurements were performed by K. Wcisło, M. Eng. at the Laboratoire de Catalyse URA 402 CNRS, University of Lille I, France; we want to thank Prof. Yolande Barbaux for enabling us to make these measurements and for the discussion. This research was supported by the State Committee for Scientific Research, KBN under the project No 3 TO9A 128 09.

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