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The Activity of True Cr_2O_3–Al_2O_3 Solid Solutions in Dehydrogenation

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The dehydrogenation of isobutane to isobutene over a series of chromia–alumina solid solutions was studied. The catalytic activity and stability to deactivation were determined.

Intrinsic activities, defined as the molar conversion to isobutene per unit area of catalyst, were compared. The curve shows a marked maximum for Cr_2O_3-rich solid solutions. Concerning Al_2O_3-rich samples, α-phases are nearly inactive, whereas γ-phases exhibit relatively high activities. Stability decreases from Al_2O_3-rich to Cr_2O_3-rich solid solutions.

This result suggests, rather unexpectedly, that the substitution of phases with a low content of chromia for the rich phases detected in usual dehydrogenation catalysts would be beneficial.

The mechanism of dehydrogenation and deactivation is discussed in terms of the chromium ions of various charges present in the solid solutions. It is concluded that Cr^{2+} ions are probably responsible for the initial high activity; this activity is very rapidly inhibited. The useful dehydrogenating centers are the Cr^{3+} ions. The slow deactivation process is probably initiated by ion pairs containing at least one Cr^{3+} ion. In Al_2O_3-rich α solid solutions, substantially no surface Cr ions are present, because of the strongly covalent character of α-phases. They are practically inactive. γ-Phases probably exhibit less covalent character, explaining their higher activity.

INTRODUCTION

The chromium oxide–aluminum oxide system has been known for many years to catalyze dehydrogenation. It has been used in commercial processes. In the dehydrogenation of hydrocarbons, rapid deactivation of the catalyst takes place, and the process is carried out in cycles, with the dehydrogenation run being followed by reactivation in an oxidizing atmosphere. Typical cycles last from 15 min (Houdry process) to 2 hr (Phillips process).

Usual chromia–alumina dehydrogenation catalysts, prepared either by gel precipitation, wet mixing, or impregnation, are treated at high temperatures, currently 600°C or above. It can be expected that, under these conditions, chromia and alumina are partially transformed to solid solutions. Some results on supported Cr_2O_3 catalysts substantiate this hypothesis (*1–3*).

Dehydrogenations are relatively simple reactions. If deactivation is overlooked, it can be considered that the catalyst acts as a mono-functional one. If this assumption is correct, one chemical species among the various substances present in the catalytic mass should be the true catalyst. More precisely, it could be expected that one special compound would display the optimum catalytic properties and the other

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substances would just impair the overall activity, selectivity, and resistance to fouling. Because the catalytic properties of the simple oxides, chromia and alumina, are very unsatisfactory, it may be assumed that some combination of them, for example some solid solution with a given composition and structure, is the ideal catalytic agent.

Numerous investigations have been devoted to chromia-containing catalysts (*4*). But few fundamental studies of the catalytic properties of Al_2O_3–Cr_2O_3 solid solutions have been performed (*5–8*), probably because it is very difficult to produce these solutions in a sufficiently dispersed form for measurable action.

The present investigation was an attempt to make such a study.

Dehydrogenation of isobutane was chosen as a test reaction. It might become a really important industrial process. As a test reaction it has the advantage of giving rise to practically no side reaction, contrary to dehydrogenation of normal butane, where several olefin isomers, or even diolefins, are produced.

EXPERIMENTAL METHODS

I. *Preparation of the Samples*

As mentioned above, the main experimental difficulty is to prepare chromia–alumina solid solutions having both a well-defined structure and a sufficiently large surface area. These requirements are somewhat contradictory. The purity and homogeneity of the solid solutions depend strongly on the synthesis temperatures and starting materials. There is no doubt presently that the phase diagram in the α-Al_2O_3–Cr_2O_3 system exhibits a continuous series of solid solutions (*9–15*). But obtaining such solid solutions requires the use of high synthesis temperatures, especially when starting from heterogeneous reagents as mechanical mixtures of the simple oxides. Low temperature (less than 800–900°C) decomposition of the hydroxides produces samples with large surface area. Such a preparation method led some authors to believe that the system exhibited an immiscibility gap (*16*). Our own results (*17*) show that solid solutions with compositions ranging from low Cr_2O_3 content to over 50% mol Cr_2O_3 form only with difficulty at low temperatures.

We succeeded in meeting both requirements simultaneously (*14, 17, 18*) by using a method very similar to that of Pâris and Pâris (*19*), namely the thermal decomposition of mixed oxalato-complexes, $(NH_4)_3[(C_2O_4)_3Al_{1-x}Cr_x]$, $3H_2O$. It turned out that, for some compositions, partial segregations occurred when the temperature of calcination was too low. This led us to synthesize three series of solid solutions by the nearly instantaneous decomposition of the mixed salts at 900, 1050, and 1200°C, with the last series covering only a limited composition range. The starting oxalato-complexes, of suitable composition and contained in flat silica crucibles, were introduced rapidly into the oven previously heated to the decomposition temperature. Decomposition times were respectively 2, 2, and 1 hr. The powdery product was crumbled and passed through a 30 mesh sieve (grain diameter less than 0.5 mm). All samples were subjected to X-ray diffractometry and BET surface area measurement. The results are summed up in Table 1. Our values for the lattice parameters of the α solid solutions have already been published (*14*). They are in excellent agreement with the recent data of Stone and Vickerman (*15*).

II. *Apparatus*

The apparatus is of the flow type. It consists of two identical independent circuits. Two quartz reactors, one in each circuit, are located horizontally, side by side, in a tubular furnace. One reactor contains the catalyst bed; the other one, without catalyst, is for reference. The furnace temperature is 588 ± 2°C. Each reactor is fed with isobutane at a constant rate of 300 cm^3 min^{-1}.

The volumes of gases flowing out during unit time spans are measured in water-sealed tanks. Product gases are sampled in glass bulbs and analyzed chromatographically.

TABLE 1

CRYSTALLOGRAPHIC AND SURFACE AREA DATA

Prep. temp (°C)	Cr_2O_3 (mole %):	0	10	20	30	35	40	50	60	65	70	80	90	100
900	Phases	γ	γ (low intens.)	γ (low intens.) + very small amt α	$\gamma + \alpha$		α + small amt γ	α	α		α	α	α	α
	S_s (m^2 g^{-1})	3.9	6.7	3.1	8.6		11.6	22.3	12.7		8.14	7.4	8.3	7.2
1050	Phases	$\gamma + \theta$ + small amt α	$\gamma + \alpha$ + small amt θ	α + small amt γ and θ	α	α	α	α	α	α		α		
	S_s (m^2 g^{-1})	12.4	28.5	20.0	7.35	5.35	5.6	4.5	4.4	4.3		5.25		
1200	Phases	α	α	α										
	S_s (m^2 g^{-1})		7.8	4.6										

III. Experimental Procedure

The oxide samples, in powder form, are thoroughly mixed with 14 g of powdered fused silica with a grain size between 0.08 and 0.5 mm. This mixture constitutes the catalytic bed. The reference reactor merely contains 14 g of silica. The powdered bed is pressed gently to avoid channeling during the catalytic test and the remaining space in the reactors is filled up with coarse-grained carborundum. Fused silica and carborundum turned out to be completely inert under working conditions. Because of this inert filling, thermal cracking and dehydrogenating side reactions in the gas phase are kept at a very low level; the extent to which these reactions take place is checked in the reference circuit.

Valid activity measurements can be obtained only if all impurities from the catalyst surface, in particular water and carbon, are carefully removed. Satisfactorily reproducible measurements (about 5%) are obtained if the following pretreatment is performed: heating in air during 6 hr at 770°C, followed by gradual cooling from 770 to 588°C for 1 hr in nitrogen. Catalytic tests began immediately after this cooling.

IV. Initial Intrinsic Activity and Stability

Since a carbon deposit forms on the surface of the catalyst during the dehydrogenation run and progressively inhibits the reaction, the activity must be measured near the beginning. The isobutene yield after 2 min is taken as the initial activity.

It is necessary here to define the various quantities used for expressing the results. Let c be the conversion of isobutane, i.e., the ratio of the number of moles of isobutane converted to the number of moles in the feed. Let ρ be the isobutene yield, i.e., the proportion of the feed converted to isobutene, and S selectivity. Then:

$$\rho = c \cdot S. \tag{1}$$

The initial activity A^0 of the catalyst is the difference between the overall yields in the reactor containing the catalytic bed and in the reference reactor:

$$A^0 = \rho^0 - \rho^0_r. \tag{2}$$

In order to compare exactly the initial activities of the various oxides, differences in specific surface area must be taken into account. A contact factor τ_i has to be defined. It is the ratio of the total surface area $\mathcal{S}_t$ of the catalyst sample (m^2) to the isobutane flow D (moles sec^{-1}):

$$\tau_i = \frac{\mathcal{S}_t}{D}. \tag{3}$$

The reverse ratio corresponds to the number of isobutane moles coming into contact with a unit surface area during unit time.

Except for solid solutions prepared at 900°C with a high Cr_2O_3 content, the sample weight was chosen so that the isobutene yield was less than 20%. Under these conditions, the activity A^0 is nearly proportional (less than 10% error) to the total surface area $\mathcal{S}_t$, and consequently to τ_i, since D remains constant in all experiments.

It is thus possible to define a new quantity, the initial intrinsic activity A^*:

$$A^* = \frac{A^0}{\mathcal{S}_t}. \tag{4}$$

The stability of the catalyst, i.e., its resistance to deactivation during the dehydrogenation run, is represented by the time $t_{1/3}$ needed for the catalyst to lose one third of its initial activity A^0.

The initial intrinsic activity A^* and the stability $t_{1/3}$ will be the kinetic quantities used for characterizing the different Al_2O_3–Cr_2O_3 solid solutions.

RESULTS

I. Overall Picture

The experimental results obtained with the oxides synthesized at 900°C are presented in Fig. 1. The same trends are also observed with the other series of oxides.

All catalyst samples deactivate during the reaction, at different rates according to composition. The higher the chromium content, the quicker the deactivation. For chromium-rich oxides, the deactivation is particularly rapid during the first minutes.

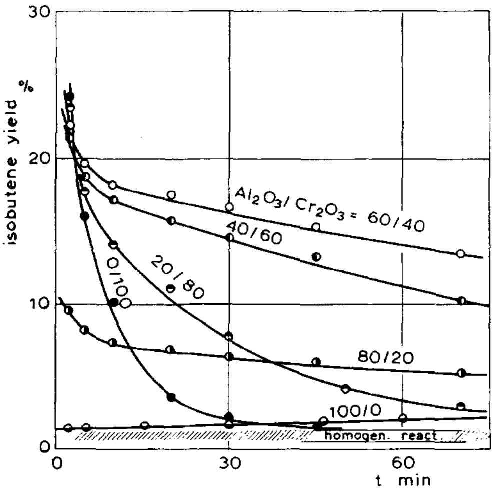

FIG. 1. Overall isobutene yield versus time for various Al_2O_3–Cr_2O_3 samples prepared at 900°C.

It should be noted that, as a consequence, a considerable error is introduced in the estimation of the initial activity.

A chromatographic analysis shows that, except for isobutene, all reaction products are formed at identical rates in the reference reactor and in the reactor containing the catalyst. They are probably formed by homogeneous reactions, since, to the accuracy of our measurements, the amount of reaction products increases with the empty space in the reference reactor (*18*). These by-products are: methane ($<0.6\%$); ethane (traces); propane ($<0.4\%$); propene ($<1.5\%$). (The values in parentheses indicate the maximum yield obtained, under experimental conditions, with reactors filled with inert material.) The proportion of the by-products, which could not be accounted for by the homogeneous reactions, is less than 0.4% of the isobutene feed.

II. Initial Intrinsic Activity

The initial intrinsic activities A^* of the various oxides mentioned in Table 1 are plotted in Fig. 2. The intrinsic activities of oxides of the same composition in two different series do not coincide. Below mole 40% Cr_2O_3, this is necessarily the case, because the crystallographic composition of the samples is very different (Table 1). For higher Cr_2O_3 contents, accurate measurement of the initial activity is more difficult. The difference in specific surface area of the samples in the series prepared at 900 and 1050°C introduces differences in the accuracy with which the measurements can be made.

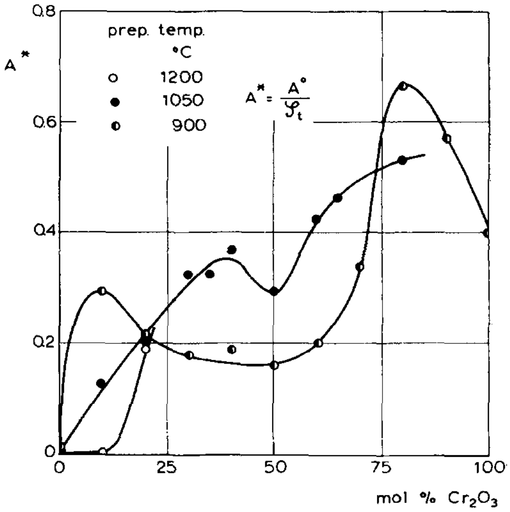

FIG. 2. Initial intrinsic activity A^* of various Al_2O_3–Cr_2O_3 samples: A^* is given here as the isobutene yield A^0 divided by the total surface S_t. This value, multiplied by the factor 1.25×10^{-4}, gives the initial intrinsic activity in moles min^{-1} m^{-2}.

In order to present comparable results, Fig. 3 has been plotted (*20*). It presents two curves, one for γ, the other for pure

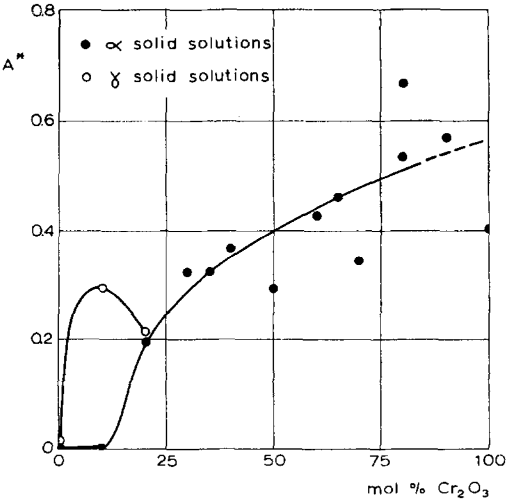

FIG. 3. Initial intrinsic activity A^* of γ and a series of α solid solutions with comparable surface area: A^* is expressed as in Fig. 2.

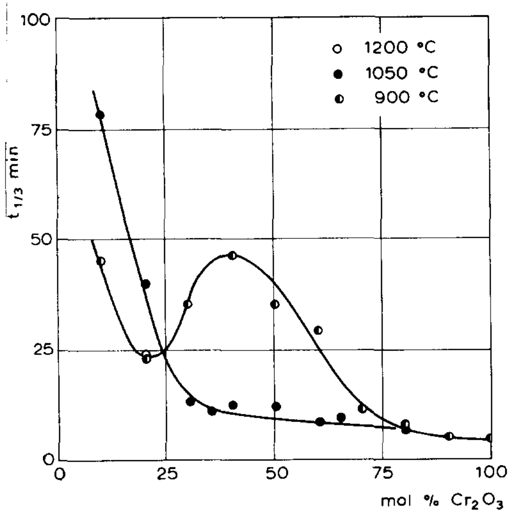

FIG. 4. Stability $t_{1/3}$ of the various Al_2O_3–Cr_2O_3 samples.

α solid solutions. The curve for α solid solution has been obtained by excluding the results corresponding to samples with a relatively high surface area (more than 12 $m^2 g^{-1}$) and by using only those with a surface area between 4.3 and 8.3 $m^2 g^{-1}$.

The curves imply two important facts. First, α-phases with a low Cr_2O_3 content are completely inactive, whereas γ-phases exhibit a marked activity. Secondly, the activity of α solid solutions increases rapidly beyond mole 10% Cr_2O_3. Inaccuracy due to rapid fouling of the catalyst for high Cr_2O_3 contents prevents precise conclusions from being drawn. It seems, however, that the activity increases up to pure Cr_2O_3.

III. Stability

The stabilities $t_{1/3}$ of all the samples used in our experiments are plotted in Fig. 4. Taking only the γ solid solutions and the pure α solid solutions having low surface area, the curve in Fig. 5 is obtained (*20*). A steady increase in stability is observed when the Cr_2O_3 content decreases.

DISCUSSION

Our results, obtained with catalysts quite different from those investigated by most previous researchers, can be used for a more precise identification of the active component in chromia–alumina dehydrogenation catalysts and for a better analysis of the various catalytic processes involved. Since our catalytic system, namely solid solutions, is different from industrial catalysts, valid conclusions may be drawn only if the reactions taking place on both systems are identical in quality and similar in velocity. The fulfillment of this condition means that we do not measure any irrelevant phenomenon. The comparison in Table 2 between the catalytic characteristics of our solid solutions and industrial catalysts shows that overall activities ρ

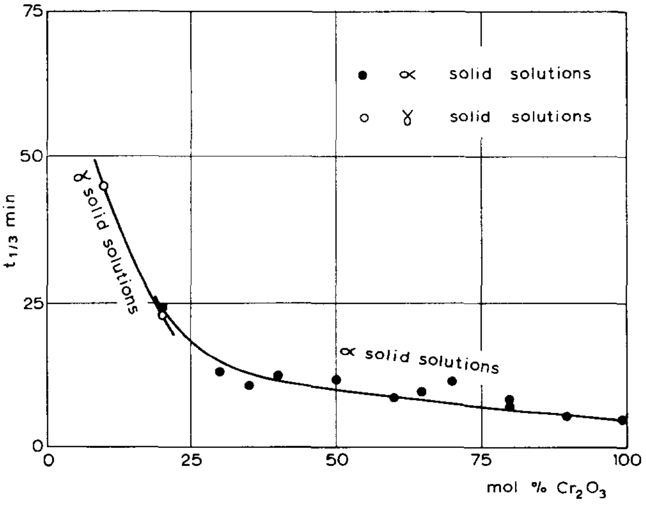

FIG. 5. Stability $t_{1/3}$ of γ and α solid solutions.

and stabilities $t_{1/3}$ do not differ enormously. The differences are not much greater than between two industrial catalysts. Specific (per unit mass) or intrinsic (per unit surface area) activities are similar to, or greater than, those of industrial catalysts. Industrial catalysts always contain a small amount of alkali metals. The presence of potassium in our solid solutions markedly improves their catalytic properties (Table 2), as it does in industrial systems. An analysis of the gas products gives the same result on all catalysts, i.e., practically only isobutene is formed.

We now proceed to the discussion. The conclusions drawn by the different authors concerning the active species in dehydrogenation and the mechanism of this process disagree in many respects (*1, 21–32*). Some authors (*21, 22*) are of the opinion that the catalytic process is related to the presence of defects created in the lattice by the reduction of Cr^{6+} ions at the beginning of the dehydrogenation cycle. This would confirm hypotheses made by Dowden (*34*). Other authors, like Slovetskaya and Rubinshtein (*33*) and Slovetskaya *et al.* (*35*) ascribe the catalytic activity to the Cr^{2+} ions. Several authors consider that the incompletely coordinated Cr^{3+} ions are the true active centers (*1, 32, 36–42*).

In typical experiments reported by numerous authors, the olefin yield first increases, goes through a maximum after a few minutes, then decreases (*39, 43, 44*). During the first minutes, a marked increase in the temperature (often nearly 50°C) of the catalyst is observed. This phenomenon is attributed to the reduction of hexavalent to trivalent chromium (*43, 44*).

The reduction of chromium ions by the hydrocarbon produces water and carbon dioxide. These products desorb only slowly from the catalyst. Their progressive desorption is assumed to set free the active sites and to cause the activity increase (*38, 39, 43, 45*). As a matter of fact, a certain parallelism is observed between the hydrated state of the surface and the time necessary to reach the maximum activity. In particular, this time is reduced at higher temperature, because of the quicker desorption of water (*38, 45*).

The loss of catalytic activity during the dehydrogenation run is generally believed to be caused by the covering of the surface with carbonaceous material, often referred to as "coke," which probably is a more or less dehydrogenated polymeric material. Most authors think that the acid sites are responsible for olefin polymerization [see for example, Ref. (*46*)]. This process is believed to occur by an acidic carbonium ion mechanism. However, it should be mentioned that in opposition to this, Shen-

TABLE 2

COMPARISON OF THE CATALYTIC CHARACTERISTICS OF Al_2O_3–Cr_2O_3 SOLID SOLUTIONS AND INDUSTRIAL DEHYDROGENATION CATALYSTS

Catalyst		Composition								
Phase	Calc temp Oxal. complex (°C)	Al	Cr	K	S_s ($m^2 g^{-1}$)	Total wt (g)	ρ (5 min)	ρ/total wt	ρ/S_{total}	$t_{1/3}$ (min)
α	650	50	50	0	135	6.8	47.8	7.03	0.052	
α	900	50	50	0	22.3	7.0	21.9	3.13	0.140	35
γ	900	80	20	0	20.0	5.0	19.25	3.85	0.192	39.5
$\gamma + \theta$	1050	88.2	9.8	2	35.0	6.0	47.6	7.94	0.226	45
Girdler G 41					206	4.0	14.4	3.60	0.017	44
Harshaw Cr 1404 P (powder)					90	4.0	29.3	7.32	0.081	>85
Procatalyse ACR 3					93	4.0	29.55	7.38	0.079	36

lrik *et al.* (*43, 45*) found that the formaion of coke is the result of a reaction oncurrent to dehydrogenation, i.e., the dsorbed activated complex might either lesorb and form an olefin molecule or olymerize into carbonaceous material.

Taking advantage of the use of our well-lefined solid solutions without a carrier, ve shall try to give additional arguments for the identification of the active sites for dehydrogenation and coke formation and for the elucidation of the mechanism of these reactions.

We will first discuss the dehydrogenating activity. It is known that Cr_2O_3 is a semiconductor of type *p* in oxidizing, and of type *n* in reducing atmosphere (*27*). When contacted with a hydrocarbon, e.g., butane, at high temperature (480°C), the *p* semiconductor instantaneously becomes *n* (*47*). When superficially reduced by hydrogen, Cr_2O_3 adsorbs much oxygen and little hydrogen; the reverse is observed on oxidized Cr_2O_3 (*40*). The adsorption of oxygen causing the formation of chromium ions with a valency higher than 3 is responsible for *p* type semiconductivity. The *n* type semiconductivity in the reducing atmosphere is caused by the formation of ions with low valency, namely Cr^{2+}, on the surface.

The catalytic properties of reduced or oxidized Cr_2O_3 in reactions other than dehydrogenation are dissimilar, i.e., reduced Cr_2O_3 is highly active in hydrogen–deuterium exchange, and in ethylene hydrogenation at −78°C; whereas oxidized Cr_2O_3 is totally inactive (*48*). This inactivity is probably caused by the chemisorbed oxygen layer, which obscures the active chromium ions. At −78°C, the surface of the oxidized catalyst is not altered by the reducing atmosphere. Voltz and Weller (*48*) observed that the excess oxygen can be removed near 500°C, after which treatment the catalyst begins to be active in the hydrogen–deuterium exchange.

Very little is known concerning Al_2O_3–Cr_2O_3 solid solutions. Nevertheless, one important result (*49*) is mentioned here because it is essential for our discussion. It was obtained by Hensler and Henry (*50*) and Eremenko and Belnish (*51*) on α solid-solutions and by Chapman *et al.* (*52*) and Bremer and Stach (*53*) on coprecipitated chromia–alumina catalysts. The semiconductivity, of type *p* or *n* according to the atmosphere, decreases when the chromium content decreases. It thus appears that the tendency of superficial oxygen to leave the surface of Cr_2O_3 decreases in the solid solutions.

Pure alumina has no semiconductivity. The adsorption of oxygen and hydrogen on superficially reduced or oxidized γ-alumina is much smaller than on Cr_2O_3 (*40*). The desorption of the surface oxygen being very small, the surface is much the same in the reducing or in the oxidizing atmosphere.

The semiconductivity results indicate that two types of cations must be present on the surface of reduced Al_2O_3–Cr_2O_3 solid solutions, i.e., Cr^{2+} and Cr^{3+}. But these results do not suggest which one is the most active in dehydrogenation. Two phenomena contribute to the overall decrease of the activity when the chromium content of the solid solutions decreases. First, progressive dilutions of the chromium ions diminishes the number of chromium sites on the surface. Secondly, the oxygen layer is more firmly attached on the surface. The surface is more similar to that of alumina, which is irreducible. When the Cr_2O_3 content goes below mole 10%, the catalytic activity falls to zero, because no chromium ions remain available. The situation is sketched in Fig. 6b,c,d.

The higher activity of a γ solid solution could be explained by the difference in the lattice energy of the γ and α forms and the correlative difference in bond energy between the surface and the chemisorbed oxygen. The γ form is a metastable oxide of a spinel type, with a marked ionic character, while the α form is stable at all temperatures and possesses a strong covalent character. Oxygen is necessarily less strongly bonded on the surface of the γ form. More chromium ions are probably available (Fig. 6e).

We now come to a discussion of activity variations during a run and, more precisely, the stability of the various

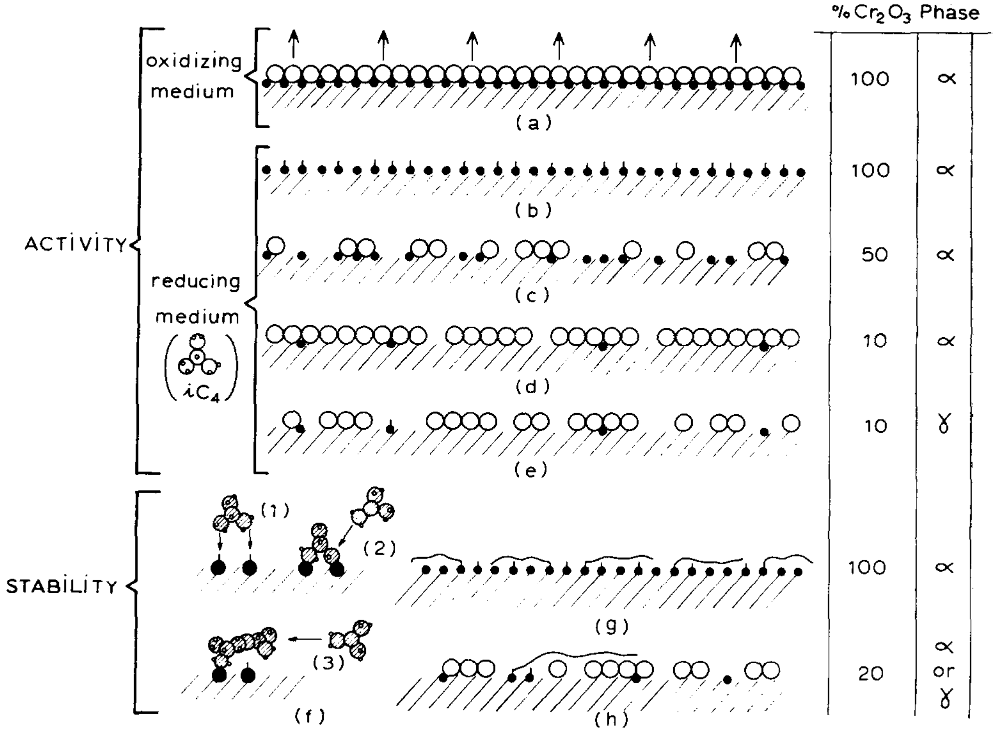

FIG. 6. Schematic diagram of the proposed surface structure of some Al_2O_3–Cr_2O_3 solid solutions near 600°C, when contacted by oxygen-containing atmosphere or by an hydrocarbon.

catalysts. For this discussion, it is useful to take arguments from the electronic theory and from the multiplet theory.

According to the electronic theory (*54*) the adsorption of a paraffin on Cr_2O_3 in its *n* state, or, more precisely, on a Cr^{2+} ion, mobilizes one electron from the catalyst. Strong chemisorption is brought about. Adsorption on a Cr^{3+} ion would only be weak chemisorption, with no participation of electrons from the semiconductor.

It is generally assumed that the multiplet theory is relevant to catalytic dehydrogenation. One possibility is that the paraffin molecule is adsorbed by two adjacent carbon atoms in a two-atom active center. This hypothesis has been put forward by Twigg (*55*) to account for the results obtained in the dehydrogenation of olefins. According to Balandin (*26*), Landau and Shchekin (*31*), paraffins would be adsorbed by their carbon atoms on the metal atoms of the catalyst. Such two-atom active centers, especially Cr^{2+}-Cr^{4+} couples on a charge-balanced surface, have been described by Stone (*56*). No indisputable picture of the adsorbed state of the paraffin or the products of the reaction can be put forward. Nevertheless, the two-atom active center necessarily includes at least one active ion or an oxygen atom attached to this ion. Supposing, for the sake of simplicity, that the active ion itself is involved, one from the couples Cr–Cr, Cr–Al, or Cr–O could be considered (Al^{3+} and O^{2-} ion on the surface are not completely coordinated and can form a weak bond with the second carbon atom; this hypothesis could be substantiated by the indisputable, although small, activity we observed with pure γ-alumina).

If the active couple includes at least one Cr^{2+} ion, the surface complexes will be fixed by strong chemisorption and will have a very long lifetime. They will be subjected to reaction with adsorbed or desorbed isobutene molecules and will form polymeric chains which will stick to the catalyst (Fig. 6g). This could account for the extremely rapid deactivation observed for Cr_2O_3-rich samples and for initial rapid, but only partial, deactivation observed in the first minutes of the run for Al_2O_3-rich samples (Fig. 1). The active couples could be the Cr^{2+}–Cr^{4+} couples mentioned by Stone for Cr_2O_3-rich solid solutions (*56*).

The slow deactivation process in the experiments with Al_2O_3-rich samples may be ascribed to the Cr^{3+} ions and, especially, to Cr^{3+} or equivalent pairs on which the surface complexes certainly have a longer lifetime. The deactivation rate on γ or on α solid solutions would decrease with the concentration of these ion pairs, thus explaining the overall trend observed (Fig. 6f,h).

Thus, Cr^{2+} would be responsible for the high initial activity and the rapid initial deactivation of all catalysts. The normal active species, especially in the Al_2O_3 rich domain, would be the Cr^{3+} ion, which is slowly deactivated.

The increase in activity usually observed with supported catalysts during the first minutes of the dehydrogenation run still has to be discussed. The first point concerns the presence of ions with valency higher than 3 on the surface of the catalysts regenerated in an oxidizing atmosphere. We measured the temperature rise during the first minute after the hydrocarbon was introduced. Pratically no temperature rise (less than 1°C) was observed with a α solid solution regenerated either under standard conditions or at lower temperatures (650°C). Temperature rises of 6–7°C were always observed with the industrial catalysts as well as with our γ solid solutions. It thus seems that a substantial amount of chromium with high valencies is present only in the latter catalyst. It is known that Cr^{5+} ions are selectively stabilized by γ- or γ-related phases containing alumina, but not by α-alumina (*57*). The EPR measurements on our solid solutions show that, after regeneration, the only signal observed with α solutions is the wide line of Cr^{3+} ($g = 1.975$, band width 200–750 G). With γ solutions, an intense sharp line ($g = 1.97$, band width 50 G) characteristic (*23, 49, 58–60*) of Cr^{5+} is observed. The thermal effect must therefore be attributed, at least most of it, to the reduction of the Cr^{5+} ions present after the regeneration of catalysts containing a γ-phase.

In our experiments, relatively little high valency chromium is expected to be present, because the calcination temperature is high (*49*). Therefore, the temperature rise is markedly less than mentioned by other workers (who have observed values up to 50°C). Water and carbon oxide formation are correspondingly lower, and the inhibition they produce could be expected to be small. This is consistent with the fact that we never noticed any increase in activity during the initial period of the dehydrogenation run.

CONCLUSION

The measurement of the catalytic activity of Al_2O_3–Cr_2O_3 solid solutions with various chemical and crystallographic compositions, together with literature results concerning semiconductivity, lead us to the following conclusions. Besides Cr^{3+}, which is certainly active, Cr^{2+} probably contributes to the overall activity. Both are active in the processes leading to the deactivation of the catalysts. It is likely that the Cr^{2+} ion is responsible for the initial superactivity and initial superdeactivation of Al_2O_3–Cr_2O_3 solid solutions. Results on γ solid solutions and on chromia-poor α solid solutions suggest that the normal active species is Cr^{3+}. Normal deactivation is probably originated by ion pairs containing at least one Cr^{3+} ion, particularly Cr^{3+} pairs. Stability increases more rapidly than activity decreases when chromium is more and more diluted in γ solid solutions, because ion pairs are correlatively held apart. We cannot conclude as to the exact nature of the active Cr^{3+} ions. The recent interpretation suggesting they would be incompletely coordinated ions (*36, 41, 42, 56, 61*) is quite acceptable. Concerning the effects observed on freshly regenerated catalysts during the initial period of the dehydrogenation run, it seems well established that they are caused by the Cr^{5+} ions, which are stabilized by γ-phases.

Our results suggest that the activity and stability of industrial catalysts could be improved. It has been shown (Table 2) that our unsupported low-surface solid solution sometimes has properties paralleling those of industrial catalysts. Actual practice is far from being adapted to synthesize the substances showing the best compromise between activity and stability, which seems to be the γ-phases with about mole 10% chromia. In particular, impregnation is likely to form mainly chromium-rich solutions and coprecipitation to form phases in too large a composition range. This is substantiated by X-ray measurements. When the presence of chromia is ascertained, the only form is α-Cr_2O_3, which is no good as a catalyst.

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