Studies on Catalytically Active Surface Compounds

XV. The Catalytic Oxidation of Ethanol on Cr/SiO₂ Catalysts and Some Relations to the Structure[1]

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Aerosil-supported chromium catalysts with Cr concentrations ranging from 10^{-4} to 1 wt% were prepared by reaction of CrO_2Cl_2 with the SiOH groups of Aerosil. For the catalytic oxidation of ethanol at 240°C the activity per gram of catalyst did not depend on the Cr concentration down to 10^{-3} wt% Cr. However, the changes in kinetic reaction order as well as activation energy E_a within the Cr concentration range indicate changes in the character of active chromium sites causing variations in the reaction mechanism. While at very low Cr content isolated Cr species specifically bound to the surface are responsible for the catalytic activity, at high Cr content the reaction occurs on "aggregated" Cr species. Since the activity depends on the pressure used to compact the catalysts the specific nature of the active isolated chromium species is connected with the globular structure of the support. © 1985 Academic Press, Inc.

INTRODUCTION

Catalytic properties of dilute supported transition metal oxides are in many cases determined both by the interaction of the ions between themselves and with the support. Activity, selectivity, and the reaction mechanism are usually influenced by the environment of the ions, i.e., their symmetry, coordination, and degree of aggregation, which depend in many cases on the concentration of the active ions (*1*). This is valid for oxidation reactions, in particular those catalyzed by dilute solid solutions and transition metal ions in zeolites, as evidenced by various papers in the literature (*2–5*).

Supported chromium catalysts, although used in oxidation processes, have greatest industrial importance in the polymerization of ethene (Phillips process). Therefore, numerous investigations on the structure of these catalysts, the type of active species, and their catalytic properties have been made. Besides the valence state of the Cr ions, one of the main questions seems to be whether isolated or "aggregated" Cr species act as catalytic active centers.

During an extensive investigation on reduced Cr/SiO₂ and Cr/SiO₂ · Al₂O₃ polymerization catalysts Hogan (*6*) found maximum activity at 30–100 ppm Cr loading. High activity of isolated Cr species is suggested and its decrease with increasing Cr content is concluded to be due to Cr aggregation. Hierl and Krauss (*7*) have shown that chromate species are present on reduced Cr(II) catalysts up to 2.8 wt% Cr. According to Iwasawa (*8*), isolated Cr species are highly active, e.g., for the hydrogenation of propene, whereas clusters are active in the oxidation of CO.

In contrast to these authors Zecchina *et al.* (*9*) and Rebenstorf and Larsson (*10*) concluded, mainly from IR measurements, that there is formation of dichromate species on SiO₂ surfaces. This conclusion is at least in partial agreement with Groeneveld *et al.* (*11*), who postulated a great variety of different aggregated Cr species, as have

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[1] For Part XIV see Ref. (*1*).

other authors (*12–14*). This short review already shows the difficulty of determining the real aggregation state of Cr ions on the surface of supports. The reasons for these divergences in the conclusions are probably connected with the use of different supports and conditions of preparation and activation.

The present paper characterizes the properties of Cr/SiO$_2$ catalysts for the oxidation of ethanol. It should be seen as a contribution to describing the influence of the pretreatment of the support and the Cr concentration on the catalytic properties and to correlating them with some structural properties.

EXPERIMENTAL

The catalysts have been prepared by reaction of CrO$_2$Cl$_2$ with the silanol groups of Aerosil according to the following equation

$$(\equiv\!SiOH)_n + CrO_2Cl_2 \rightarrow$$
$$(\equiv\!SiO)_nCrO_2Cl_{2-n} + nHCl \quad (1)$$
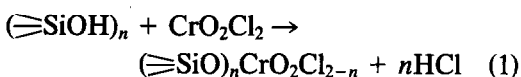
The disappearance of the strong 3750-cm^{-1} IR band of isolated SiOH groups supports Eq. (1); however, this is not meant to exclude the possibility of CrO$_2$Cl$_2$ reaction with other types of SiOH groups (geminal, vicinal, etc.). Catalysts of different composition have been obtained by variation of the SiOH group concentration and the Cr content.

The following modifications were additionally prepared: (a) samples without hydrolysis; (b) dilution by subsequent grinding with an additional amount of support; (c) extraction of chromium from the support in two steps by H$_2$O and 2N H$_2$SO$_4$.

1. Preparation conditions. Degussa Aerosil-200 ($S = 200$ m^2/g) was made into a paste with water and dried at 150°C. The particle fraction 0.6 to 1.0 mm in diameter was used. Subsequently the SiOH concentration was varied by temperature pretreatment of the Aerosil denoted as (TPA) in air for 8 h at 250, 500, and 800°C, resulting in

SiOH concentrations of 0.78, 0.58, and 0.25 mmole/g, respectively (*15, 16*). The reaction of Aerosil with CrO$_2$Cl$_2$ was performed in water-free and fresh distilled CCl$_4$ containing the desired amount of CrO$_2$Cl$_2$. The solution was boiled for some hours in the presence of a slow stream of dry air.

Choosing low Cr content (<0.5% Cr) and taking Aerosil with high SiOH concentration (TPA = 250°C) the solution decolorized indicating complete reaction of CrO$_2$Cl$_2$ with Aerosil. If the Cr content increased and/or the SiOH concentration decreased (TPA = 800°C) an increasing part of the CrO$_2$Cl$_2$ remained unreacted. After the reaction the liquid was removed by filtration and the solid was freed from CCl$_4$ by means of dried air. At low Cr content (about 0.1% Cr and less) and high SiOH concentration the catalysts were already Cl$^-$ free. All other samples had to be hydrolyzed in a stream of wet air at about 100°C to remove Cl$^-$. Finally, all samples were dried in a stream of dry air at 100°C for 8 h.

In a separate study some of these samples have been further treated by compacting them in a conventional tabletting press at desired pressures. The tablets were then crushed and the original particle fraction was used for the catalytic measurements.

2. Analysis. Chemical analysis was carried out iodometrically (Cr(VI)). The total Cr content was determined after oxidation of the samples with K$_2$S$_2$O$_8$ or in the case of low Cr concentrations in air at 200–300°C. Samples with a Cr content of 0.1% and less were analyzed colorimetrically with diphenylcarbazide. According to their solubility three kinds of species could be distinguished: Cr(VI) soluble in H$_2$O, Cr(VI) only soluble in 0.1 N H$_2$SO$_4$, and Cr(III).

3. Catalytic measurements. Investigations were carried out under gradientless conditions in a gas-circulation reactor at 220–270°C. The mean residence time was varied at constant partial pressures of ethanol to ensure a constant level of conversion (about 30%) under stationary reaction con-

ditions. Mixtures of about 1 vol% ethanol + 10 vol% O_2 in N_2 were used as reactants. The reaction products were analyzed by gas chromatography. The selectivity is expressed in percentage of reactant consumed or in terms of the accumulation rate of the products. The influence of sample compacting on catalytic properties was measured in a flow-type reactor at 240°C (total flow rate 5.6 cm³ s⁻¹, sample weight 1 g). The conversion level was held at about 40%.

4. *Spectroscopy.* ESR measurements were carried out in the temperature region between −196 and 240°C using a ZWG ERS-220 spectrometer working in the X-band. A single crystal of $CuSO_4 \cdot 5\ H_2O$ was used as quantitative intensity standard.

A Beckman DK2A spectrometer with a reflectance attachment was used for measuring UV–vis spectra. An appropriate sample of the pure support (Aerosil) served as standard.

Temperature-programmed reduction (TPR) experiments were performed in a flow apparatus with a gas mixture of 4% H_2 in N_2 at a flow rate of 0.83 liter h⁻¹ and a linear heating rate of 4 K min⁻¹. The H_2 consumption during TPR was followed by means of a heat conductivity cell. Oxidative pretreatment of the samples could be achieved *in situ* using air instead of H_2/N_2.

RESULTS

1. Catalysis

The starting activity of all catalysts is rather low and the stationary activity is only reached after a time which depends on the Cr concentration.

Catalytic results obtained in dependence on both the Cr and SiOH concentration under steady-state conditions are shown in Fig. 1. It can be seen that at 240°C the activity per g Cr increases with decreasing Cr content (Fig. 1a) (the pure support is, however, inactive) whereas the overall activity per g catalyst remains constant in a concentration range 10⁻³ to about 1 wt% (Figs. 1b, c).

In addition, it is shown that a decrease of the SiOH concentration of the support from 0.78 (TPA = 250°C) to 0.25 mmole/g (TPA = 800°C) decreases the activity over the whole Cr range. A variation of the reaction temperature gives similar curves for 220 and 240°C. At 270°C, however, the activity depends clearly on the Cr concentration (Fig. 1d). Nearly the same results were obtained if the "dilution" of chromium was carried out either by dissolving portions of Cr ions from the surface or by grinding a given catalyst with an additional amount of support (factor 10 to 100). Table 1 shows that even after a 100-fold dilution the catalyst still has the original activity per gram of catalyst. This property (positive dilution effect (2)) is observed down to 10⁻³ wt% Cr (about 10¹⁷ Cr atoms per gram).

Further lowering of the Cr content, however, caused a strong decrease of activity (Fig. 1c).

From the minimum Cr content showing still constant stationary activity and this activity value the turnover number is estimated to be

$$\frac{6.02 \times 10^{17}}{1.16 \times 10^{17}} \sim 5 \frac{\text{molecules } C_2H_5OH}{Cr_{atom} \cdot s}$$

Hogan (6) calculated a turnover number of 2.8 (molecules produced)/(active site · s) for the ethene polymerization.

Using compacted catalysts some remarkable results were obtained. At first, by applying pressure on pure Aerosil its porosity is decreased, which leads, according to Iler (17), to an increase of the coordination number of Aerosil primary particles (Table 2). Second, it is evident from Fig. 2 that the catalytic activity (expressed as conversion level) could be increased when using compacted catalysts, but the selectivity to acetaldehyde was unaffected (Table 3).

Selectivity. Ethanol is converted to final oxidation products only to low extents (max. 4% CO_2, Table 4). Selective oxidation products are acetaldehyde, acetic acid, and acetic acid ethyl ester. The ratio of the
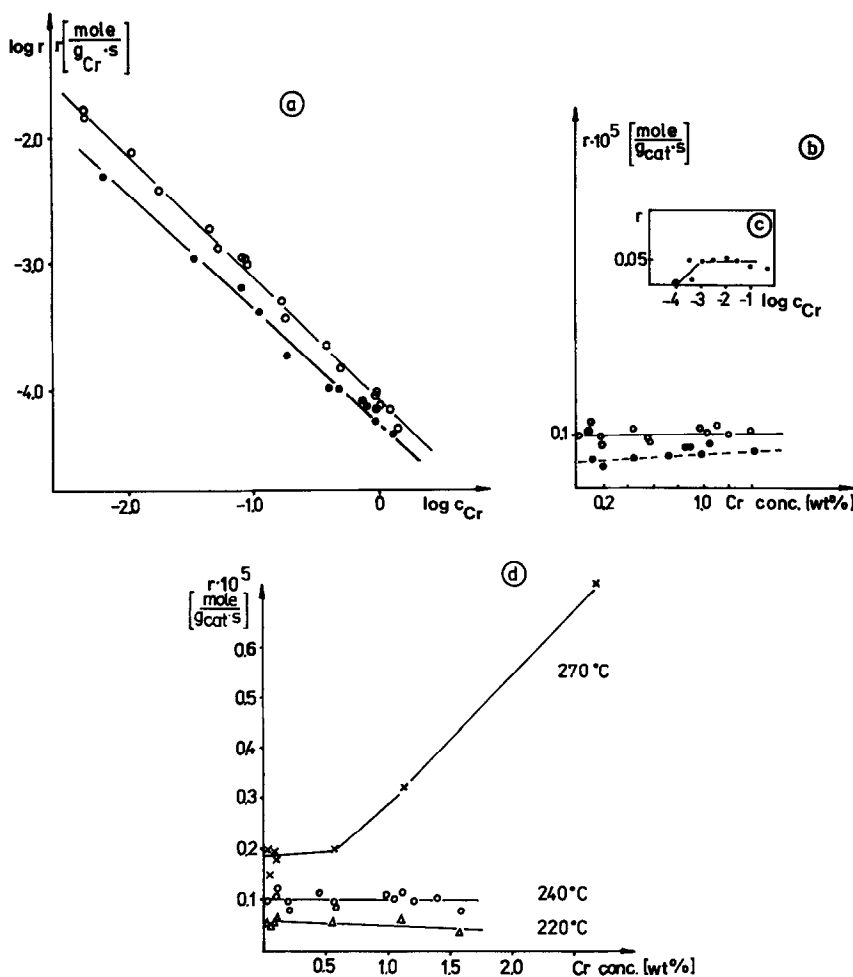
FIG. 1. Effect of the Cr concentration C_{Cr} on the steady-state activity, r (moles/g_{Cr} · s), of Cr/SiO$_2$ catalysts. Oxidation of ethanol (at 240°C): (○) TPA = 250°C and (●) TPA = 800°C. (a) Per gram Cr, (b) per gram of catalyst, and (c) as (b) for strong diluted system (TPA = 800°C). (d) Oxidation of ethanol (240°C) on Cr/SiO$_2$ catalysts. Steady-state activity r (per gram of catalyst) versus the Cr concentration at different reaction temperatures; TPA = 250°C.
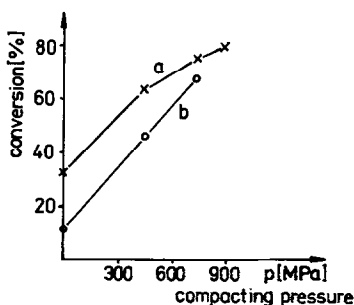

FIG. 2. Oxidation of ethanol at 240°C on Cr/SiO$_2$ catalysts. Effect of compacting the samples on the conversion. (a) TPA = 250°C, 0.005% Cr; (b) TPA = 800°C, 0.007% Cr.

first two products at about the same degree of conversion strongly depends on the Cr content (Fig. 3). At the highest Cr content nearly 70% acetaldehyde is produced whereas at lower Cr content the introduction of oxygen to form acetic acid is favored (Table 4).

When using compacted catalysts the selectivity values remain unchanged (Table 3).

Formal kinetics. The activation energies E_a were calculated for the temperature region between 220 and 270°C for catalysts

TABLE 1

Steady-State Activities for Ethanol Oxidation under Standard Conditions

TPA[a] (°C)	Additional treatment before reaction	Total Cr content (wt%)	Activity, $r \times 10^5$	
			mole/$g_{Cr} \cdot$ s	mole/$g_{cat} \cdot$ s
250	None	1.59	4.7	0.075
250	Diluted by grinding with the tenfold amount of Aerosil	0.145	54.1	0.078
250	Diluted by grinding with the 100-fold amount of Aerosil	0.013	646	0.083
800	None	0.098	58.9	0.058
800	Washed with H_2O	0.058	162.6	0.094
800	Washed with $2N$ H_2SO_4	0.037	227.1	0.084
800	Treated in air, 500°C, 5 h; then washed with $2N$ H_2SO_4	3×10^{-4}	19,090	0.057

Note. Variation of the Cr concentration of the original samples by grinding with different amounts of Aerosil or partial removing of Cr with H_2O or $2N$ H_2SO_4.

[a] Temperature of pretreatment of Aerosil.

with different Cr content from the corresponding Arrhenius plot (Fig. 4). Nearly constant E_a values of about 14 kcal/mole were found for catalysts with a Cr content up to 0.5 wt%. At higher Cr content the activation energy increases up to about 25 kcal/mole. The use of "mechanically" diluted catalysts gives the same picture as shown in Fig. 4 (circles). Figures 5a and b show the reaction velocity r versus the partial pressures of ethanol and oxygen for a series of catalysts with different Cr con-

tents. Both figures show an influence of the Cr content such that both the $n_{C_2H_5OH}$ and the n_{O_2} values increase with decreasing Cr loading.

2. Temperature-Programmed Reduction (TPR) and ESR

TPR curves of hydrolyzed catalysts show two distinct reduction rate maxima at 340–370°C (Low-Temperature Peak, LTP) and at 470–490°C (High-Temperature Peak, HTP) (Fig. 6).

TABLE 2

Influence of Compacting Pressure on the Porosity of Aerosil ($S = 200$ m²/g)

Pressure (MPa)	Pore volume, V_p (cm³/g)	Bulk volume, V_b (cm³/g)	Porosity (V_p/V_b)	Coordination number[a]
—	1.47	1.88	0.78	<4
48	1.34	1.79	0.75	<4
96	1.04	1.60	0.65	4
191	0.86	1.38	0.62	4
478	0.49	1.04	0.47	6
1000	0.33	0.89	0.37	>8

[a] Coordination number of a primary particle of Aerosil, according to Iler (17).

TABLE 3

Influence of Compacting Pressure on CH_3CHO Selectivity[a]

Pressure (MPa)	Conversion (%)	CH_3CHO selectivity (%)
0.1	42.8	32.8
454	43.9	38.9
756	40.6	38.4
756	36.5	40.0
908	43.2	36.4

[a] Cr content: 0.005 wt%; TPA = 250°C.
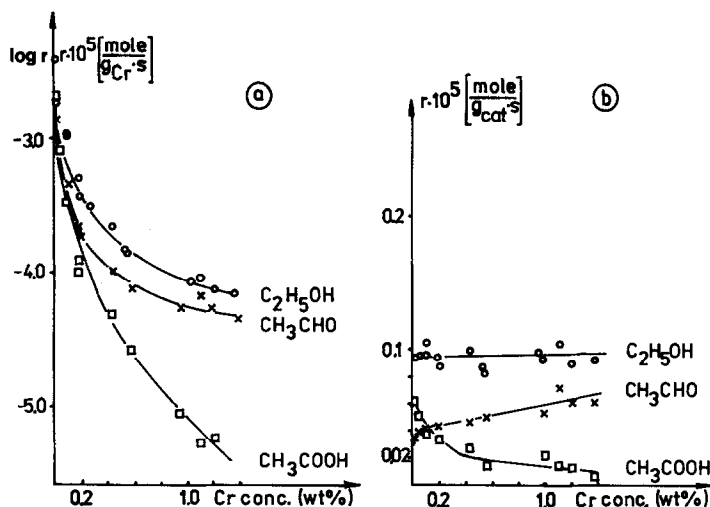
FIG. 3. Oxidation of ethanol (240°C) on Cr/SiO₂ catalysts. Activity (C₂H₅OH) and accumulation rate (CH₃CHO,CH₃COOH) versus Cr concentration (a) per gram of chromium and (b) per gram of catalyst.

The appearance and the ratio of these two TPR peaks depend, however, on the preparation conditions and the treatment of the catalysts. For hydrolyzed catalysts the intensity of the LTP decreases with decreasing Cr content (Fig. 6). Reduction of unhydrolyzed catalysts shows only the HTP, the intensity of which decreases with decreasing hydroxyl concentration of the support (Fig. 7) caused by a different degree of spontaneous prereduction of the sample (Table 5). Under the chosen TPR conditions the degree of reduction did not exceed 100% (taking full reduction of Cr(VI) to Cr(III) as 100%). The LTP can additionally be developed, however, by preadsorption of water on unhydrolyzed samples (Fig. 8). Reoxidation and subsequent reduction gives evidence that a catalyst formerly reoxidized at temperatures higher than about 320°C does not show the LTP any more (Fig. 9).

An attempt has been made to study the reoxidation of prereduced samples (500°C, 1 h reduction in H₂) volumetrically and by ESR spectroscopy. It appears from Fig. 10 that the O₂ uptake at a given temperature is higher if (i) the Cr content is low and (ii) the original SiOH concentration of the support was high (TPA = 250°C). ESR shows that these samples stabilize Cr^{5+} ions ($g_\perp$ = 1.98, $g_\parallel$ = 1.95) to a certain degree during

TABLE 4

Selectivity (in Percentage of Consumed Reactant) of Cr Catalysts for the Oxidation of Ethanol at 240°C (TPA = 250°C)

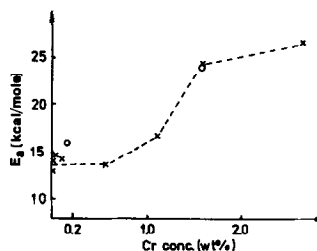| Cr content (wt%)	Oxidation of ethanol			
	% CH₃CHO	%CH₃COOH	%Ester	%CO₂
1 × 10⁻⁴	25.1	51.0	21.8	
0.005	30.2	32.3	22.0	1.9
0.05	39.8	33.1	19.1	2.6
0.1	42.4	22.3	15.7	3.4
0.19	45.1	13.1	15.6	4.0
0.44	46.4	15.2	10.9	3.5
1.21	66.8	4.1	6.4	3.4

FIG. 4. Oxidation of ethanol (240°C) on Cr/SiO₂ catalysts. Activation energy E_a versus the Cr concentration. (×) Cr conc. changed by variation of the CrO₂Cl₂ conc. during preparation. (O) Cr conc. varied by diluting a given catalyst with the desired amount of additional Aerosil.
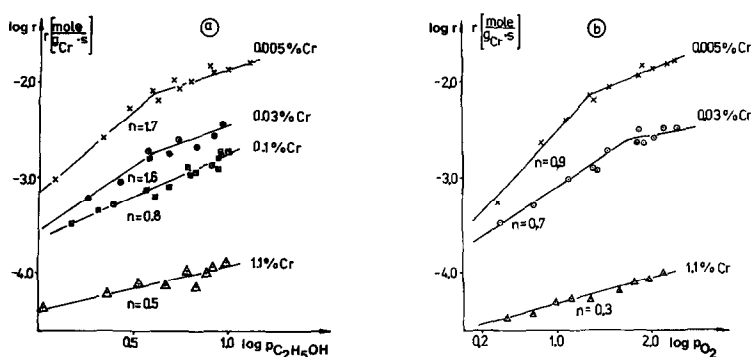
FIG. 5. Oxidation of ethanol (240°C) on Cr/SiO$_2$ catalysts Reaction order n for different Cr concentrations for (a) ethanol and (b) oxygen.

TABLE 5

Oxidation of Ethanol on Unhydrolyzed Cr/SiO$_2$ Catalysts[a]

TPA (°C)	c_{OH} (mmole/g)	Cr(VI) content[b] (wt%)	DR[c] (%)	Activity,[d] $r \times 10^5$	
				mole/g$_{Cr}$ · s	mole/g$_{cat}$ · s
250	0.78	0.097	84	103.1	0.103
500	0.58	0.086	66	70.4	0.070
800	0.25	0.05	48	38.5	0.039

[a] Influence of the SiOH concentration C_{OH} (Cr content of all samples was 0.1%).
[b] Analyzed before TPR run or catalytic reaction.
[c] H$_2$ consumption during TPR expressed as degree of reduction (DR) to Cr(III).
[d] Steady-state activity.

reoxidation (Fig. 11). The relative concentration of stable Cr^{5+}[(Cr^{5+}/Cr$_{tot}$) · 100%] is highest for samples with low Cr content and low TPA, being roughly estimated to be 6% for sample a, compared to 1.2% for sample b and about 0.1% for sample c (Fig. 11).

The main signal after preparation (i.e., without any treatment) is, however, a single broad line at $g \approx 2$, well known as the β-phase signal of clustered Cr^{3+} ions (18). Two additional signals were detected, namely that of Cr^{5+} ions (γ-phase), which
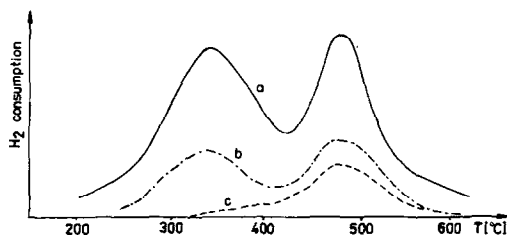

FIG. 6. TPR spectra of Cr/SiO$_2$ catalysts (TPA = 250°C). Effect of the Cr concentration on the spectra and achieved degree of reduction (DR). (a) 0.46% Cr, DR = 90%; (b) 0.21% Cr, DR = 75%; (c) 0.09% Cr, DR =80%.
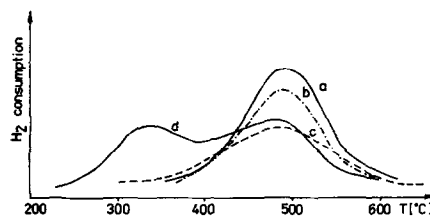

FIG. 7. TPR spectra of unhydrolyzed Cr/SiO$_2$ catalysts (Cr conc. = 0.1 wt%). Effect of the temperature of pretreatment of Aerosil (TPA) on the spectra and on the degree of reduction (DR). (a) TPA = 250°C, DR = 84%; (b) TPA = 500°C, DR = 66%; (c) TPA = 800°C, DR = 48%; (d) sample (c) after pretreatment in dry air for 2 h at 250°C before the TPR run, DR = 90%.
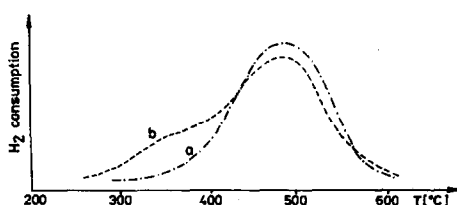
FIG. 8. TPR spectra of Cr/SiO₂ catalysts (TPA = 250°C, 0.1% Cr). Influence of moisture on the spectrum: (a) unhydrolyzed sample and (b) TPR run after preadsorption of moisture.

FIG. 10. Chemisorption of oxygen on prereduced Cr/SiO₂ catalysts (H₂, 500°C, 1 h). Change of oxidation number Δz versus the temperature of reoxidation T_{reox} calculated on the basis of the O₂ uptake (the arrows mark those points where the H₂ consumption during reduction is compensated). (a) TPA = 250°C, 0.1% Cr; (b) TPA = 250°C, 1.1% Cr; (c) TPA = 800°C, 1.1% Cr.

disappeared after storage in air, and a weak signal of isolated Cr^{3+} ions (δ-phase; $g = 3.6$–4.6). Because of overlapping of the individual signals no quantitative interpretation has been attempted. It should, however, be emphasized that after reduction the ratio of the amplitudes of the δ- to β-phase signals increases with decreasing Cr content.

3. UV–vis Reflectance Measurements

UV–vis reflectance spectra of hydrolyzed samples of low Cr content (<0.5 wt% Cr) show three characteristic absorption bands of equal intensity at 21,400–22,400 (I), 27,000–30,000 (II), and 38,000–42,000 cm⁻¹ (III) (Fig. 12, curve a). An additional shoulder (better resolved after subsequent thermal treatment in air) is observed in the visible region (~15,000 cm⁻¹) which, in agreement with chemical analysis, points to low-valence chromium ions. This band disappeared immediately after exposing the
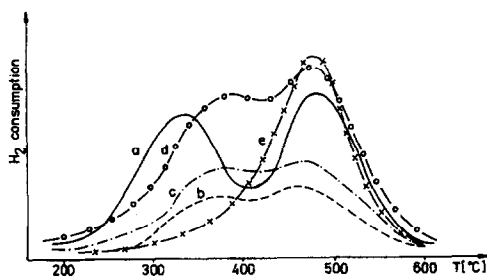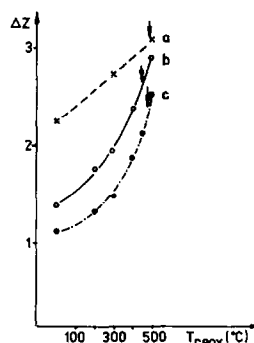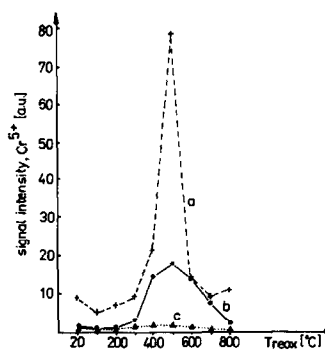
sample to wet air (Fig. 12). In the literature d–d absorption bands assigned to Cr(V) were reported at 13,000 (19) or 13,800 cm⁻¹ (20). These bands were not observed here, although the ESR measurements show a Cr^{5+} signal, the relative intensity of which is highest for low Cr content (Fig. 11). The formation of Cr(IV) ions, which according

sample	after red.	Tᵣₑₒₓ. (°C)			
		100	300	500	700
a	li-blue	light brown →		light yellow →	
b	blue-grey	grey-blue →		orange	li-green
c	blue-grey	grey-blue →		green	light-green

FIG. 11. ESR signal intensity calculated per gram Cr of the Cr^{5+} signal versus the temperature of reoxidation T_{reox} after prereduction with H₂ at 500°C. The appropriate sample colors are given below the figure. (a) TPA = 250°C, 0.1% Cr; (b) TPA = 250°C, 1.1% Cr; (c) TPA = 800°C, 1.1% Cr.

FIG. 9. TPR spectra of Cr/SiO₂ catalysts (TPA = 250°C, 0.2% Cr). Effect of the reoxidation temperature on the spectra: (a) untreated, (b) T_{reox} = 150°C, (c) T_{reox} = 250°C, (d) T_{reox} = 320°C, (e) T_{reox} = 400°C (recorded with only 50% amplification).
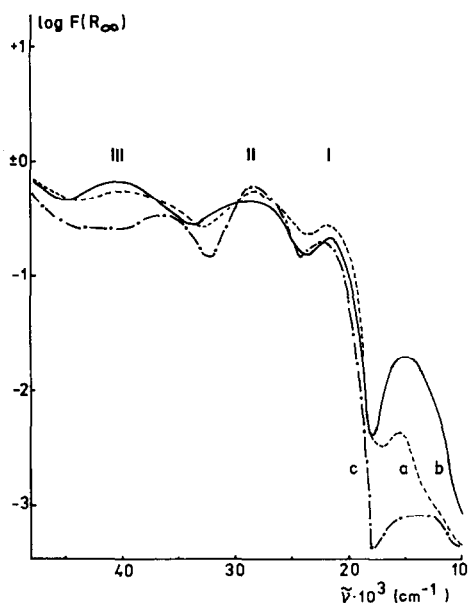
FIG. 12. UV–vis reflectance spectra after various treatments. Sample: TPA = 250°C, 0.1% Cr. (a) Untreated, (b) 5 h at 600°C in air, (c) sample (b) after adsorption of H_2O at 20°C.

to Lever (21) should absorb in the 15,000-cm^{-1} region, is excluded due to high thermal stability of the catalysts under oxidizing conditions.

DISCUSSION

Regardless of the varied Cr concentration the catalysts have nearly the same overall activity at 240°C (Fig. 1b), and consequently the activity per gram Cr is drastically enhanced with dilution (the pure support is inactive).

At first sight this result might be explained by assuming one type of Cr species being active over the whole concentration range while the increasing part of the total chromium is inactive. This assumption disagrees, however, with significant changes of the selectivity (Fig. 3), the activation energies E_a (Fig. 4), and the kinetic orders for oxygen and ethanol (Fig. 5) in dependence on the Cr loading. Whereas at least the activation energy is nearly constant in a limited concentration range up to 0.5% Cr the values for the kinetic orders both of oxygen
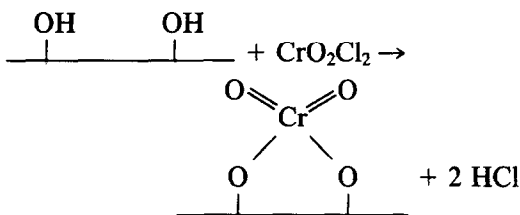
and ethanol continue growing to a certain degree even below 0.1% Cr.

These contradictions with the assumption mentioned above lead us to suggest the existence of more than one type of Cr site on the surface. This suggestion is basically in agreement with other experimental results, namely with (i) various types of Cr ions showing different solubility (in H_2O, H_2SO_4, nonsoluble) (see Table 1), and (ii) the existence of three paramagnetic Cr ions (β-, δ-, and γ-phases) proved by ESR on fresh catalysts. These results show qualitatively the variety of chromium surface species already on the fresh catalyst; they do not, however, indicate coincidence in any way.
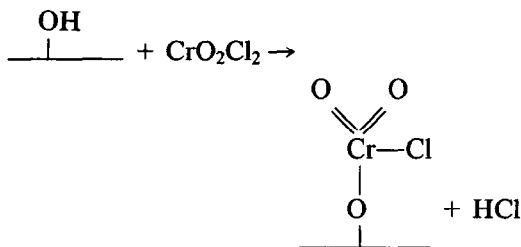
One may ask what may be stated with respect to the nature of the different Cr sites. It is known from the literature that catalysts obtained by impregnation of silica with a solution of chromic acid (6, 9) contain chromate and bichromate species besides α-chromic oxide at relatively high Cr concentrations. Often, by comparing solution spectra of K_2CrO_4 and $K_2Cr_2O_7$, UV–vis measurements were used to distinguish between chromate and dichromate species. Bands at 26,800 and 36,400 cm^{-1} were taken as evidence for chromates and those at 23,100, 28,500, and 39,000 cm^{-1} for dichromates, respectively. This method is, however, not convincing because Szabó et al. (22) have shown that a band in the 22,000-cm^{-1} region can also be obtained from various chromates. In addition, it should be expected that both chromates and dichromates give rise to similar spectra when fixed to the surface of a support (12). On the other hand, McDaniel (14, 23) was able to show that the gas phase reaction between CrO_2Cl_2 and the SiOH groups on silica which had been calcined at temperatures up to 400°C results in the formation of a surface chromate; this species, however, is stabilized on the surface only in the absence of moisture.

This is in good agreement with the TPR results shown in Figs. 6 and 7. At low Cr

concentration and high SiOH concentration only the HTP at 470°C appears (Fig. 6c) which corresponds to more than 80% Cr (VI) ions being reduced to Cr(III). As the unhydrolyzed sample taken for the TPR run of Fig. 7a was Cl$^-$-free already without hydrolysis it is concluded that relatively strongly bound chromate surface species are formed, according to the reaction:

$$
\begin{array}{cc}
\text{OH} & \text{OH} \\
\underline{\quad|\quad\quad\quad|\quad} & + \text{CrO}_2\text{Cl}_2 \rightarrow
\end{array}
$$

$$
\begin{array}{c}
\text{O} \diagdown \diagup \text{O} \\
\text{Cr} \\
\diagup \diagdown \\
\text{O} \text{O} \quad + 2\ \text{HCl} \\
\underline{\quad|\quad\quad\quad|\quad}
\end{array}
$$

On samples with low SiOH concentration (TPA = 800°C) chemical analysis proved that unreacted Cr–Cl bonds remained to a large extent (14):

$$
\begin{array}{c}
\text{OH} \\
\underline{\quad|\quad\quad} + \text{CrO}_2\text{Cl}_2 \rightarrow
\end{array}
$$

$$
\begin{array}{c}
\text{O} \text{O} \\
\diagdown\diagup \\
\text{Cr}\text{—Cl} \\
| \\
\text{O} \quad + \text{HCl} \\
\underline{\quad|\quad\quad}
\end{array}
$$

Contact of these species with moisture leads to partial hydrolysis of the surface compounds followed by some "aggregation" of Cr(VI) species (24); these were more easily reduced than the isolated ones and caused the LTP at 340°C (Fig. 8). The absence of this LTP in Figs. 7c and d and the amount of H$_2$ consumed during the TPR run shows that these catalysts were partly reduced already prior to TPR. Pretreatment of the fresh sample in dry air at 250°C caused the LTP to appear (Fig. 7d). Although the origin of this partial prereduction is still unclear, it is not suggested, on the basis of the experimental results, that it is caused by thermal decomposition.

As can be seen from Fig. 9, only at temperatures higher than 320°C does reoxidation of the reduced aggregated species lead

to their conversion into chromate species. Apparently this is connected with the splitting of Cr–O–Cr bonds. Similar reduction experiments with H$_2$ in a closed circulating system were presented by Hogan (6) and Finch (13) on CrO$_3$/SiO$_2$ · Al$_2$O$_3$ catalysts (2.5% Cr) showing a single reduction rate maximum at about 300–350°C for a dry catalyst, activated in air at 540°C. A second peak at 410°C appears for the same catalyst containing 5% water. This is interpreted (6) as a two-stage reaction, that is, part of the Cr(VI) is converted to Cr$_2$O$_3$ in the presence of moisture. The aggregation of Cr ions in the presence of moisture and the high reducibility of these high-valent Cr species easily forming Cr(III) ions agree well with the results of the present paper. At the experimental conditions used here a special TPR peak for reduction of Cr(III) to Cr(II) could never be observed. The different temperatures of the TPR peak maxima corresponding to the chromate species must be due to the differences in the sample composition and in the experimental conditions as well. Finch (13) was able to show that both the decrease of the Cr concentration and of the Al$_2$O$_3$ portion in the support shift the TPR peak maxima to higher temperatures. In addition, it was shown by Groeneveld et al. (11) for a Cr/SiO$_2$ catalyst that the rate of reduction is low below 330°C and reaches a maximum at about 450°C.

Thus, from the TPR measurements it may be concluded firmly that the lower the Cr content and the higher the SiOH concentration on the surface the more likely is the formation and stabilization of chromate species. This parallels the changes in catalytic activity and points therefore to chromate species as the active sites of the reaction at low Cr concentration, whereas at increasing Cr concentration less active "aggregated" chromates (di- or polychromates) become important.

As water is formed during the reaction, causing "aggregation" of chromium ions, one would expect the highest reaction rate
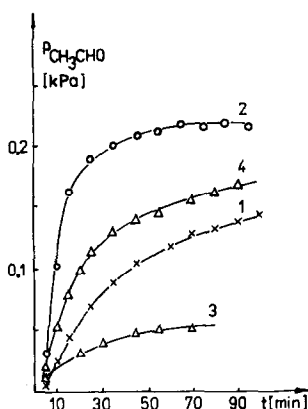
FIG. 13. Oxidation of ethanol on Cr/SiO_2 catalysts at 240°C. Acetaldehyde concentration versus reaction time. (1) TPA = 250°C, 0.01% Cr; (2) TPA = 250°C, 0.1% Cr; (3) TPA = 800°C, 0.1% Cr; (4) TPA = 800°C, 0.1% Cr (H_2O added).

at the start of reaction on samples containing only (or almost only) chromate species. Unfortunately, this could not be observed because, regardless of the method of preparation, all samples need a formation period for reaching stationary activity (Figs. 13, 14). Reduction of the chromate species, possibly necessary for reaching stationary activity, cannot be the reason for the formation period because it occurs nearly instantaneously with ethanol under these conditions. This suggests that the active sites still have to be formed during this time of formation, as reported for the polymerization reaction of ethene (25).

If the active site has to be searched for among the chromate species it is evident that it should be a particular one comprising a minor part of them. This can be concluded also from the constant overall activity of the catalysts down to Cr contents of about 10^{-3} wt%. ESR measurements point to Cr(V) ions that are stabilized like the chromate species particularly on samples with high SiOH concentration during thermal treatment at about 500°C in the presence of oxygen (Fig. 11). From the characteristic colors visible during reoxidation (Fig. 11) it is obvious that samples stabilizing the Cr(V) ion became orange–yellow in

the temperature region from 400 to 600°C whereas the others change already to green. After increase of temperature the color turns to green, too, indicating thermal decomposition to Cr(III). This oxygen loss connected with the green color starts already at about 400–500°C if the SiOH concentration is low. The portion of Cr(V) ions detected by ESR grows with decreasing Cr content, comprising about 6% in the sample with 0.1 wt% Cr (TPA = 250°C) (Fig. 11). Interestingly, this concentration is in the vicinity of the lowest Cr content (0.001%) where the catalysts still have constant overall activity (Fig. 1c).

The results obtained by UV–vis spectroscopy, in particular the band at about 15,000 cm⁻¹ (Fig. 12), are in agreement with the ESR measurements. Since this band cannot be ascribed to Cr(IV) or Cr(VI) ions (see Experimental) it appears to be most likely that this absorption may be caused by Cr(V) ions.

Besides this outstanding stability of the Cr^{5+} valence state observed by ESR and UV–vis under (re-)oxidizing conditions, the active sites should show some peculiarities relevant for the working catalyst. It seems reasonable to see them in a specific interaction with the support. As is well known, Aerosil has a globular structure
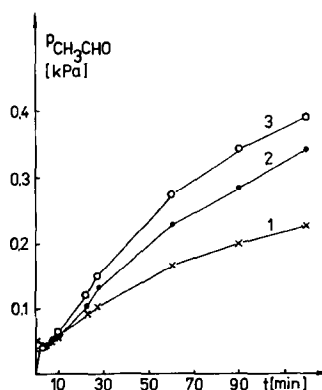

FIG. 14. Oxidation of ethanol on Cr/SiO_2 catalysts. Yield of acetaldehyde versus the reaction time in dependence on the compaction pressure (sample TPA = 250°C, 0.005% Cr). (1) Unpressed sample, (2) $p = 756$ MPa, (3) $p = 908$ MPa.

and, for the kind of Aerosil used in this investigation, the mean diameter of the primary particles is 12 nm. The resulting number of particles amounts therefore to about 10^{17}/g Aerosil. This number is of the same order of magnitude as that of active, isolated Cr species. This suggests that Cr species situated at sites where two primary particles come into contact with each other may be the centers of high catalytic activity. The peculiarity of these sites could be a significant higher probability to form Cr surface compounds bound to the surface by two or three Cr–O–Si bonds. Though being a rough conclusion, its validity is checked by compacting the catalysts, which increases the packing density of the primary particles. According to Iler (17) the compacting should increase the number of contact sites and consequently, according to our model, the number of active Cr species in a given catalyst.

From Fig. 2 it is indeed evident that the compacted catalysts show enhanced activity. Obviously, the number of active centers have been increased but, as concluded from the unchanged acetaldehyde selectivity (Table 3), not their character. As shown in Figs. 13 and 14, both compacted and uncompacted catalysts exhibit the same activity for the acetaldehyde formation at the start of the reaction. The enhanced activity of the compacted catalyst is only reached after a certain reaction time interval. It is supposed that during this interval the chromium ions may migrate to the contact areas of the primary particles. This migration process possibly includes reduction–reoxidation reactions, hydrolytic splitting of surface bonds and also changes in the dispersion of chromium. Figure 14 shows how various factors affect this process. These experimental facts support the idea of active sites as isolated Cr ions specifically bound to the surface at the contact areas of the primary particles of Aerosil. Moreover, as was shown before, ESR measurements revealed the existence of Cr(V) ions, the number and behavior of which were close to those of the active centers. If one assumes a threefold bound$\equiv$Cr^{5+}=O, the formation of which may have higher probability at the contact areas of the Aerosil primary particles, it immediately becomes evident that this species should be relatively stable to further oxidation. This, however, does not necessarily mean that the active Cr ion is five-valent because the oxidation state of the active Cr ions cannot be specified on the basis of the results of this investigation.

Hence, disregarding the valence states of the corresponding chromium species, it is reasonable to assume the existence of three different active sites, as detailed below.

A. Isolated chromium species fixed in the vicinity of the contact areas of the Aerosil primary particles: They determine the overall activity at very low chromium content and favor the formation of acetic acid. Their absolute concentration decreases with increasing chromium loading due to "aggregation."

B. Remaining isolated chromium centers of lower activity producing acetaldehyde: these centers, however, are not favored by a particular interaction to the surface, in contrast to those in A. Their concentration increased in a limited concentration range with increasing chromium content.

C. Chromium centers on which the acetaldehyde formation is favored: These centers should consist of more than one chromium ion ("aggregated" species); their concentration increases parallel to the chromium loading.

The amounts of chromium respectively occupying these three sites are determined by the total chromium content of the catalysts and the original SiOH group concentration of the support. Up to 240°C mainly sites A and B contribute to the overall activity which, as the sum of both sites, is constant. At reaction temperatures above 240°C (shown here for 270°C) site C species contribute at higher Cr content making the activity dependent on the Cr loading.

Obviously with growing surface concen-

tration the catalysts contain more and more "aggregated" Cr ions, at least in the presence of water or under reaction conditions. It should be emphasized at this point that the temperature dependence of the β-Cr^{3+} ESR signal differs from that of α-Cr_2O_3 (the Néel-point at about 34°C is not observed) showing that despite the "aggregation" the catalysts contain well-dispersed chromium, though clusters of about 5 nm or smaller are possibly present (26). These aggregated species obviously represent the active surface centers catalyzing the oxidative dehydrogenation by a usual redox mechanism. The lower the Cr content the more grows the role of isolated Cr ions bound in the assumed way to the surface, and the more predominates another type of reaction mechanism. The lower activation energy and the significant increase of the reaction orders for both ethanol and oxygen point to some kind of coordinative mechanism characterized by a transition state including both ethanol and oxygen.

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