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The Dehydrogenation of Ethane over Chromium Catalysts

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The nature of the active sites for ethane dehydrogenation over chromium supported on silica gel has been studied by infrared spectroscopy, together with kinetic measurements. Low nuclearity A-type chromium(II) ions are believed to be the active sites for ethane dehydrogenation on Cr/SiO_2 catalysts. Higher dehydration temperatures increased the concentration of active A-type chromium(II) ions. The apparent activation energy was the same for different dehydration temperatures, which indicates that the number but not the type of site changed upon dehydration at elevated temperatures. The active A-type chromium(II) sites were selectively poisoned by carbonaceous deposits during the dehydrogenation of ethane. Turnover frequencies, based on the calculated number of surface chromium atoms, were similar for Cr/SiO_2, Cr/Al_2O_3, and α-Cr_2O_3, but a CrY zeolite was essentially inactive since chromium ions remain in the +3 oxidation state.

INTRODUCTION

Both supported chromium and α-Cr_2O_3 are known to be active catalysts for the dehydrogenation of alkanes. Numerous attempts have been made to identify the active site. Chromium(II) appears to be the oxidation state favored by several investigators (*1–3*), although Cr(III) has also been proposed (*2, 4–6*). Ashmawy (*2*) evaluated ethane dehydrogenation over chromium-alumina catalysts, and proposed that both Cr(II) and Cr(III) are active for the reaction, although Cr(II) is the more active ion. Konig and Tetenyi (*4*) have studied the dehydrogenation of ethane on α-Cr_2O_3, and have identified coordinatively unsaturated Cr(III) ions as the active sites.

The nuclearity of the active sites has also been investigated. From an infrared study of nitric oxide and carbon monoxide adsorbed on chromia/alumina, Peri (*7*) has provided evidence for isolated and paired Cr(II) ions. He suggested that paired Cr(II) ions may be needed for hydrocarbon dehydrogenation and dehydrocyclization. Zecchina *et al.* (*8*) claim that dichromate groups are mainly formed on the surface of CrO_3/SiO_2 catalysts after calcination in flowing O_2. These dichromate species produce pairs of Cr(II) ions after reduction in CO. McDaniel (*9*), however, argues that the data can equally well be interpreted as evidence for the formation of surface chromate ions.

Probe molecules such as carbon monoxide and nitric oxide provide insight into the oxidation state and available coordination sites of supported metal ions. Of particular interest in the present study were carbonyl complexes which form when CO is adsorbed on a fully reduced surface of chromium on silica gel. Recently, Garrone and co-workers (*10–12*) have proposed that carbonyl bands at 2182 and 2192 cm^{-1} are due to Cr(II) ions coordinated to 2 and 3 oxygen atoms of the surface, respectively. These divalent chromium ions are labelled A-type and B-type chromium(II) ions, respectively. The evidence from the present study suggests that the coordinatively unsaturated A-type chromium(II) ions, which result in the carbonyl band at 2182 cm^{-1}, are responsible for ethane dehydrogenation. Emphasis in this study was placed on silica as a support because of its favorable

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transmission in the infrared region, and because the various forms of Cr(II) on silica are reasonably well understood.

EXPERIMENTAL

Materials. The CrO_3 employed in this study was MCB guaranteed grade and the α-Cr_2O_3 and $CrCl_3 \cdot 6H_2O$ were Fisher Scientific certified grade. Davison grade 57 silica gel and Conoco Catapal SB grade alumina were used as supports. The NaY zeolite was supplied by Union Carbide.

All of the gases used in this study, with the exception of the He (AIRCO), were purchased from Matheson. Carbon monoxide (ultra-high purity grade) and helium (high purity grade) were further purified by passing through an oxygen scavenger prior to use. Oxygen was extra dry grade and was used as received. Nitric oxide and ethane (C.P. grade) were purified by repeated vacuum distillation at the freezing point of *n*-pentane (−135°C). Water impurities in the gases were removed by passing them through a silica-gel trap. Liquid water was purified by using the freeze–pump–thaw technique.

Sample preparation. Silica-supported chromium(VI) catalysts were prepared by impregnating the silica gel with chromic acid solutions. The silica gel was washed in HCl, dried in air at 140°C, and calcined in flowing O_2 at 500°C. Typically 10 g of SiO_2 was mixed with 25 ml of H_2O which contained the appropriate amount of Cr. The resulting concentrations were 0.1, 0.26, 0.52, 1.0, and 2.1 wt% Cr, as determined by standard chemical methods. Similarly, an alumina-supported chromium(VI) catalyst was prepared by impregnating alumina with chromic acid solution. The resulting concentration was 0.50 wt% Cr.

A sample of CrY was prepared from a NaY zeolite by aqueous ion exchange with a solution of $CrCl_3$. The solution was stirred at 25°C for 12 h. The zeolite was then separated from the solution by filtering, repeatedly rinsed with deionized H_2O, and finally dried at 100°C. The zeolite catalyst was stored in a hygrostat over a saturated ammonium nitrate solution. The resulting chromium concentration was 0.50 wt%.

Spectroscopic methods. Infrared (ir) spectra were obtained using a Perkin Elmer Model 580 spectrophotometer. The spectra were recorded with the sample at room temperature. Samples were prepared by grinding the catalyst to a powder and pressing it into wafers, typically 10 mg cm^{-2}. Samples were pretreated in a Vycor cell fitted with KCl windows.

Catalytic studies. Initial rates for ethane dehydrogenation were determined in a recirculation reactor. The gases were recirculated using a Pyrex pump which had a maximum pumping speed of 300 cm^3/min. The total volume of the recirculation system was 315 cm^3. Gas samples from the kinetic studies were analyzed using an online gas chromatograph. The sampling volume was 1/125 of the total volume of the system. The temperature in the reactor was monitored using a subminiature chromel-alumel thermocouple placed outside, but touching the middle section of the reactor. These temperatures were corrected to those of the catalyst bed.

A 50 mg sample of catalysts (20–42 mesh) was placed in a U-tube reactor. The catalysts were dehydrated *in vacuo,* oxidized in O_2 (200 Torr) and reduced in CO (50 Torr). The oxidation step was omitted with the CrY zeolite. After this pretreatment, the dehydrogenation of ethane was carried out. The partial pressure of ethylene were monitored as a function of time, and the initial rate of reaction was determined by a numerical method. The experimental data were fitted to a function with a maximum degree of smoothness by using a natural cubic spline interpolation method. The initial rate of reaction was determined from the first derivative of the spline function in the first data interval.

The deactivation and reactivation studies of the catalysts were conducted using a flow system. Gas samples taken during the

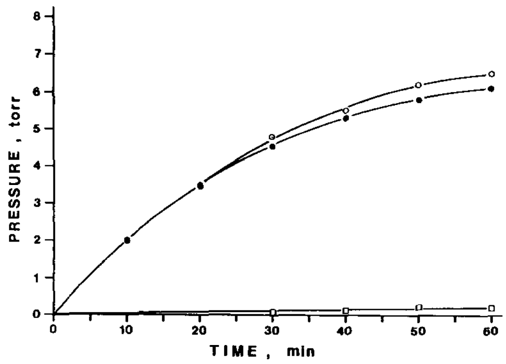


FIG. 1. Partial pressure of the products of ethane dehydrogenation versus time of reaction in a recirculation reactor. The catalyst was 0.52 wt% Cr/SiO_2 heated *in vacuo* at 885°C, oxidized in O_2 at 495°C and reduced in CO at 495°C for 90 min: ●, C_2H_4; ○, H_2; □, CH_4.

flow experiments were analyzed using an online gas chromatograph. The chromium catalysts (ca. 0.5 g, 0.5 wt% Cr) were dehydrated *in vacuo* at the appropriate temperature, oxidized in flowing O_2 (760 Torr) and reduced in flowing CO (760 Torr) at 495°C. After this pretreatment, a mixture of He and C_2H_6 was passed through the reactor, and the C_2H_6 conversion was monitored as a function of time on stream. Reactivation was achieved by passing O_2 through the catalyst at 495°C for 3 h.

H_2 evolution studies. In this study, the amount of Cr(II) in the reduced catalysts was determined by analyzing the amount of H_2 evolved after oxidation of the reduced catalysts with water at 595°C. The vapor pressure of water was 25 Torr. The gas phase was sampled and analyzed for H_2 by GC every 20 min until the H_2 pressure was constant.

RESULTS

Catalytic studies. Figure 1 shows the results obtained when C_2H_6 at a pressure of 100 Torr was recirculated over a reduced Cr/SiO_2 catalyst at 495°C. No induction period was observed, even when an oxidized Cr/SiO_2 catalyst was used. The amount of each product increased continuously with reaction time. All of the catalysts were deactivated before the gas phase reached the equilibrium conversion of 12 Torr of C_2H_4 at 495°C. In general very good selectivities (>94%) were observed for the formation of ethylene. No CH_4 was observed when Cr/Al_2O_3 catalysts were used, but small amounts of CO and CH_4 were observed when α-Cr_2O_3 was the catalyst. After subtracting the amount of gases lost during the sampling, mass balances were found to be 100% for both hydrogen and carbon, including coke. The carbonaceous deposit on the surface was oxidized in O_2 at 595°C, forming CO_2 in the gas phase.

Table 1 shows the effect of the support on the catalytic activity of chromium catalysts for ethane dehydrogenation, along with the BET surface areas and the amount of coke on a deactivated catalyst. The turnover frequencies decreased in the order Cr/Al_2O_3 (585°C) > Cr/SiO_2 (885°C) > α-Cr_2O_3; however, if one considers the errors involved in determining the number of surface chromium ions, it is probably not possible to make a distinction between the activities of the three catalysts. No reaction was observed when a CrY zeolite was used. The marked decrease in activity for the Cr/Al_2O_3 sample between vacuum treatment at 585 and 885°C may be the result of a transformation of the alumina from the γ-phase, which occurs at 850°C.

The color of the deactivated catalysts remained light blue, and the amount of coke found was quite small. For the Cr/SiO_2 samples the coke required to poison the catalyst was only ca. one carbon atom per chromium atom. The infrared evidence (see below) indicates that this coke is selectively deposited on the active site. In order to determine whether the deactivation was indeed a result of coke poisoning rather than thermal instability of a reduced form of Cr, two catalysts were heated under vacuum at 885°C and reduced in CO at 345°C for 1.5 h. One of these catalysts was exposed to C_2H_6 at 495°C, and an initial rate of 76 μmole C_2H_4 min^{-1} g cat^{-1} was observed. The other

TABLE 1

Effect of the Support on the Catalytic Activities of Chromium Catalysts[a]

Catalyst	Treatment[b]	Surface[c] area (m^2/g)	Initial rate		Coke wt% C/g cat
			$\frac{\mu\text{mole } C_2H_4}{\text{min} \times \text{g cat}}$	$\frac{\text{molecules } C_2H_4}{\text{sec} \times \text{surf. Cr}} \times 10^2$	
Cr/SiO_2[d]	Vac 485°C	—	18.7	—	0.10
Cr/SiO_2	Vac 585°C	246 ± 10	28.9	0.48[g]	0.11
Cr/SiO_2	Vac 885°C	234 ± 10	66.6	1.11[g]	0.12
Cr/Al_2O_3[e]	Vac 485°C	—	52.5	—	0.12
Cr/Al_2O_3	Vac 585°C	245 ± 10	94.9	1.64[g]	0.14
Cr/Al_2O_3	Vac 885°C	—	8.1	—	—
α-Cr_2O_3	Vac 485°C	16 ± 3	92.3	0.53[h]	0.24
Cr(III)Y[f]	Vac 485°C	—	None	—	—

[a] Reaction condition: $P_{C_2H_6} = 100$ Torr, Temp = 495°C.

[b] The catalysts were heated *in vacuo* at the indicated temperature, oxidized in O_2 at 495°C, and reduced in CO at 495°C for 90 min before the reaction in a recirculation system. Cr(III)Y was not oxidized after heating *in vacuo*.

[c] Surface areas were calculated on samples that were only dehydrated.

[d] 0.52 wt% Cr.

[e] 0.5 wt% Cr.

[f] 0.5 wt% Cr.

[g] Assuming all the chromium on the surface.

[h] The number of surface atoms was calculated as 1.084×10^{19} atoms m^{-2}.

catalyst was heated *in vacuo* at 685°C for 4 h before the reaction was carried out at 495°C; the initial rate was 57 μmole C_2H_4 min^{-1} g cat^{-1}. Thus, a 25% decrease in activity resulted from the thermal treatment, which is much less than the decline in activity observed during the catalytic reaction over the same period.

The effect of the dehydration temperature on the catalytic activity is further described in Fig. 2 for a 0.5 wt% Cr/SiO_2 catalyst, reduced at 495°C. A maximum in the initial rate was observed when the catalyst was heated *in vacuo* at 815°C. The maximum rate was 77.3 μmole C_2H_4 min^{-1} g cat^{-1}. Within experimental error the BET surface area was constant over this temperature range.

In order to determine the relationship between catalytic activity and the oxidation state of the chromium ions on the surface, separate samples of 0.52 wt% Cr/SiO_2 were reduced in CO at 345°C for different lengths of time. Then, 100 Torr of C_2H_6 was recirculated over the catalysts at 495°C. The catalytic activity for ethane dehydrogenation increased with reduction times up to 30 min. For a sample reduced less than 1.5 h in CO small amounts of CO and CO_2 were observed during the reaction with C_2H_6,

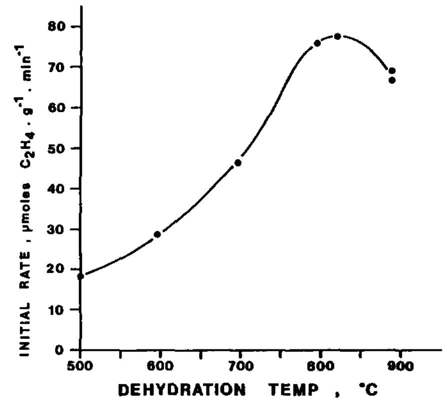


FIG. 2. Effect of dehydration temperature on initial catalytic activity. Samples of 0.52 wt% Cr/SiO_2 were heated *in vacuo* at the temperature indicated, oxidized in O_2 at 495°C and reduced in CO at 495°C for 90 min.

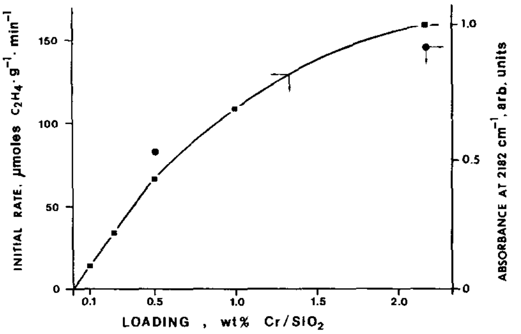


FIG. 3. Effect of chromium loading on initial catalytic activity. Samples of Cr/SiO_2 were heated *in vacuo* at 885°C, oxidized in O_2 at 495°C, and reduced in CO at 495°C for 90 min: ■, initial reaction rate; ●, infrared absorbance at 2182 cm^{-1}.

which indicates that the reactant further reduced the catalyst. The amount of CO and CO_2 decreased with reduction time. In addition, separate samples of 0.5 wt% Cr/SiO_2 were reduced in CO for 1.5 h at different temperatures. Following reduction the temperature was raised to 495°C and 100 Torr of C_2H_6 was recirculated over the reduced catalysts. The catalytic activity for ethane dehydrogenation did not change appreciably with reduction temperature over the range 350–500°C.

The nuclearity of chromium in the active site was evaluated by studying several Cr/SiO_2 catalysts having different loadings of Cr. These catalysts were pretreated in the same manner before exposure to 100 Torr of C_2H_6 at 495°C in the recirculation reactor. The results are shown in Fig. 3, in which the initial rate is reported as a function of Cr loading. The activity increased linearly with respect to Cr loading up to 0.5 wt%, but at higher loadings the increase was nonlinear. A similarly activated silica gel blank was also exposed to 100 Torr of C_2H_6 at 495°C, and no reaction was observed.

The rate of catalyst deactivation, the limit of deactivation, and the ability of the catalyst to recover the initial activity were studied in the flow reactor. Ethane (100 Torr) diluted in He was passed over the catalysts at 495°C, and the activity was monitored for several hours. After this time, the catalyst was regenerated in flowing O_2 and reduced in flowing CO. Again, C_2H_6 was passed over the catalysts at 495°C. The results appear in Fig. 4, in which the percentage conversion of C_2H_6 is reported for fresh and regenerated Cr/SiO_2 and Cr/Al_2O_3 catalysts. The more active Cr/SiO_2 catalyst exhibited a rapid deactivation to the level of the less active Cr/SiO_2 catalyst. Most of the

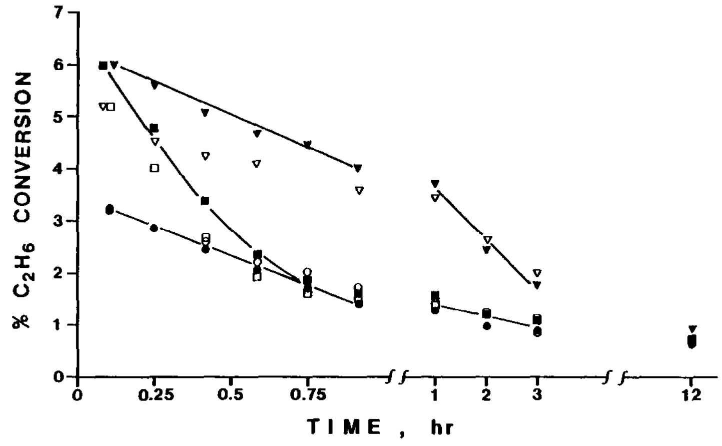


FIG. 4. Catalyst deactivation in a flow reactor at 495°C: ●, Cr/SiO_2 activated *in vacuo* at 585°C; ○, previous sample regenerated in O_2 at 495°C; ■, Cr/SiO_2 activated *in vacuo* at 885°C; □ previous sample regenerated in O_2 at 495°C; ▼, Cr/Al_2O_3 activated *in vacuo* at 585°C; ▽, previous sample regenerated in O_2 at 495°C. $W/F = 1 \times 10^{-2}$ g/min/cm^3.

TABLE 2

Kinetic Parameters for Ethane Dehydrogenation on Cr/SiO_2 Catalysts

Catalyst[a]	Treatment	n	E_a[b] (kcal/mole)
$Cr(VI)/SiO_2$	Vac 585°C, O_2 495°C, CO 495°C	0.74 ± 0.05	27 ± 1
$Cr(VI)/SiO_2$	Vac 885°C, O_2 495°C, CO 495°C	0.64 ± 0.05	28 ± 1

[a] 0.52 wt% Cr.

[b] E_a = apparent activation energy.

activity could be regained by activation in O_2. The Cr/Al_2O_3 catalyst did not experience as rapid an initial decline in activity; however, after 12 h the activities of the three catalysts were approximately equal. In an attempt to avoid the rapid deactivation of the Cr/SiO_2 catalysts dehydrated at 885°C, H_2O or CO_2 was added to the C_2H_6 feed. Water produced an even faster deactivation of the catalyst, while CO_2 had no effect.

Using the Weisz–Prater criteria (*13*) it was shown that diffusion was not a limiting factor in the reaction rate. As an indication of the quality of the kinetic data it is also significant that the initial rates obtained from the recirculating reactor and from the flow reactor, obtained by extrapolating the curves in Fig. 4 to zero time, were very similar.

Rate law. The rate law for ethane dehydrogenation on Cr/SiO_2 catalysts was evaluated using the recirculation reactor and the initial rate method. The pressure dependency, as well as apparent activation energies, were determined using the following rate equation:

$$\text{Rate} = kP^n_{C_2H_6}. \qquad (1)$$

Here, $k = A\exp(-E_a/RT)$ and E_a is the apparent activation energy.

The kinetic parameters for ethane dehydrogenation over the Cr/SiO_2 catalysts are summarized in Table 2. An average reaction order of 0.69 ± 0.05 was the same, within the experimental error, for both dehydration temperatures. The apparent activation energy was also the same within experimental error, with an average value of 27.5 kcal $mole^{-1}$.

Infrared studies. Infrared spectroscopy was utilized to investigate the effect of the dehydration temperature on the surface state of the 0.52 wt% Cr/SiO_2 catalyst. Samples were heated *in vacuo* at 585 or at 885°C. The samples were then oxidized in O_2 at 495°C for 1.0 h, and reduced in CO for 1.5 h at the same temperature. An infrared band present at 3745 cm^{-1} due to surface silanol groups was considerably less intense for samples dehydrated at 885°C than for those dehydrated at 585°C.

Upon exposure to 40 Torr of CO at 25°C for 0.5 h, both samples exhibited bands in the carbonyl stretching region. For the sample dehydrated at 585°C, only one band at 2190 cm^{-1} appeared as depicted in Fig. 5b, while for the sample dehydrated at

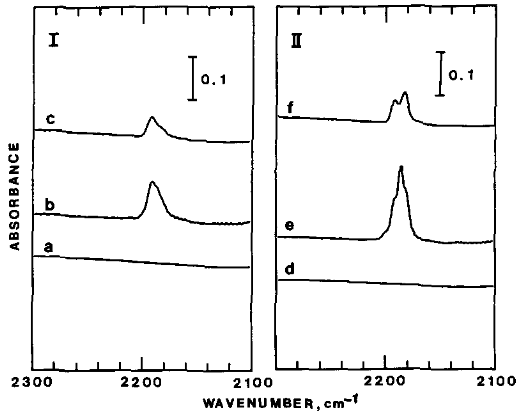


FIG. 5. Infrared spectra of CO adsorbed on 0.52 wt% Cr/SiO_2. Panel I: (a) sample heated *in vacuo* at 585°C, oxidized in O_2 at 495°C, and reduced in CO at 495°C for 90 min; (b) sample subsequently exposed to 40 Torr of CO at 25°C; (c) after CO evacuated for 3 min at 25°C. Panel II: (d) sample heated *in vacuo* at 885°C, oxidized in O_2 at 495°C and reduced in CO at 495°C for 90 min.; (e) sample subsequently exposed to 40 Torr of CO at 25°C; (f) after CO evacuated 3 min at 25°C.

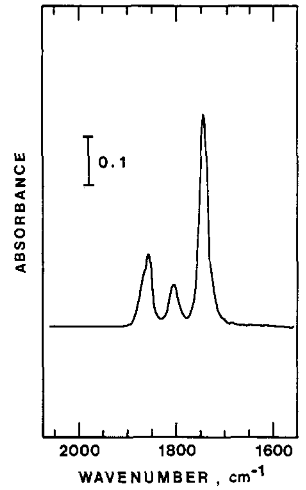


Fig. 6. Infrared (difference) spectrum of NO adsorbed on 0.52 wt% Cr/SiO_2 dehydrated at 885°C, oxidized in O_2 at 495°C, and reduced in CO at 495°C for 90 min. Sample was exposed to 15 Torr of NO at 25°C, and NO was briefly evacuated.

885°C, a triplet was easily observed at wavenumbers of 2192, 2185, and 2182 cm^{-1} as depicted in Fig. 5e. After evacuation for 3 min, the intensity of the 2192 and 2182 cm^{-1} bands decreased by ca. half. For the sample dehydrated at 585°C, a clear shoulder appeared beside the 2190 cm^{-1} band as depicted in Fig. 5c, while for the sample dehydrated at 885°C, the band at 2185 cm^{-1} disappeared as depicted in Fig. 5e. All of the CO bands were removed by evacuation at 25°C for periods of 1 to 5 h. For comparison, the relative amplitude of the band at 2182 cm^{-1} for the samples activated at 885 versus 585°C was 3, whereas the ratio of activities (Table 1) for the same two samples was 2.3.

Upon exposure to 15 Torr of NO for 1 h, both samples exhibited bands in the nitrosyl stretching region. The spectra were not affected by evacuation of the gas phase NO. For the sample dehydrated at 885°C, three bands appeared at 1858, 1807, and 1745 cm^{-1} as depicted in Fig. 6. A shoulder is apparent at 1869 cm^{-1}. For the sample dehydrated at 585°C (spectrum not shown) bands appeared at 1865, 1804, and 1744 cm^{-1}.

The background infrared spectrum of the activated catalysts in the region 1600–2000 cm^{-1} revealed two broad bands, at 1870 and 1645 cm^{-1}. These absorptions, detected in previous studies, have been assigned to overtones and harmonics of the SiO stretching mode (*14–16*). Exposure of a similarly activated silica gel blank to CO or NO at 25°C resulted in an unperturbed background spectrum.

In an attempt to relate the infrared bands to the oxidation state of the chromium ions on the surface of the catalyst, a sample was dehydrated at 885°C, oxidized in O_2 at 495°C for 1.0 h, and reduced in CO at 345°C, rather than at 495°C, for 1.5 h. Upon exposure to 40 Torr of CO, the infrared bands were the same as those shown in Fig. 5e, although less intense.

The effect of C_2H_6 and reaction products on the surface of Cr/SiO_2 catalysts was determined by reducing in CO at 345°C and then contacting with C_2H_6 at 495°C for 5 min. Upon exposure to CO or NO, the infrared bands increased in intensity with respect to the sample which was not contacted with C_2H_6, thus it is evident that ethane rapidly reduced any oxidized chromium to Cr(II).

The infrared spectra of adsorbed CO also showed that the species responsible for the band at 2182 cm^{-1} was selectively poisoned during the deactivation of the catalyst. A Cr/SiO_2 catalyst, dehydrated at 885°C, was reduced in CO at 495°C for 90 min and then exposed to C_2H_6 at 495°C for 5 min. After exposure to 40 Torr of CO at 25°C, the bands at 2192, 2185, and 2182 cm^{-1} were observed. However, after the sample was exposed to C_2H_6 at 495°C for 3 h to simulate a deactivated catalyst, and then exposed to CO, the intensity of the band at 2192 cm^{-1} did not change, while the band at 2182 cm^{-1} almost disappeared.

The nuclearity of chromium on the surface was studied by observing the effect of loading on the infrared spectra. A sample of 2.1 wt% Cr/SiO_2, in addition to the 0.52 wt% sample noted above, was dehydrated at 885°C, oxidized in O_2 at 495°C for 1.0 h, and reduced in CO at 495°C for 1.5 h. Upon exposure to CO or NO, the infrared bands increased in intensity with increased loading, but the increase was not proportional to the amount of chromium for the 2.1 wt% sample. The intensity of the band at 2182 cm^{-1} is plotted as a function of loading in Fig. 3.

A sample of CrY zeolite was heated *in vacuo* at 485°C and exposed to CO at 495°C for 1.5 h. No bands were observed in the hydroxyl stretching region. Upon exposure to CO, two weak bands appeared at 2169 and 2122 cm^{-1}. Upon exposure to NO, two bands appeared at 1898 and 1722 cm^{-1}, each possessing shoulders at 1883 and 1747 cm^{-1}, respectively. These bands agreed well with those reported in a similar study by Pearce *et al.* (*17*). An attempt to obtain ir spectra of CO and NO on Cr/Al_2O_3 was not successful as the sample had very low transmittance in the region 4000–1600 cm^{-1}.

H_2 evolution. Quantitative determinations of the amount of Cr(II) formed during the reduction of a Cr/Al_2O_3 catalyst has been obtained by Slovetskaya *et al.* (*18*) using the reaction

$$2CrO + H_2O \rightleftharpoons Cr_2O_3 + H_2 \qquad (2)$$

for which the amount of H_2 formed at 600°C was measured. We believe that this is a more accurate means of determining the amount of Cr(II) than the usual technique whereby the amount of CO_2 formed during the reduction of the catalyst with CO is measured.

Several samples of Cr/SiO_2 were reduced using different pretreatments and then exposed to water vapor at high temperatures. The amount of H_2 evolved during the oxidation step was measured. The results appear in Table 3, in which the mole ratio (H_2/Cr) is reported for the several pretreatment conditions. The ideal value for this mole ratio, assuming all the chromium in the catalyst is reduced to Cr(II), is 0.5 according to reaction (1). Based upon this stoichiometry the percentage of chromium as Cr(II) may be determined, and the results are given in Table 3. All of the 0.52 wt% samples underwent considerable reduction, even with CO at 345°C; however, the percentage of Cr(II) in the 2.1 wt% sample was much less. Presumably this is a result of clustering of the chromium on the latter sample to a less reducible form such as Cr_2O_3.

TABLE 3

Values of nH_2/nCr for Samples of Cr/SiO_2

Loading (wt%)	Treatment[a]	$\frac{\text{moles } H_2{}^{b}}{\text{moles Cr}}$	% Cr(II)
0.52	Vac 585°C, O_2 495°C, CO 495°C	0.48	96
0.52	Vac 885°C, O_2 495°C, CO 495°C	0.46	92
0.52	Vac 885°C, O_2 495°C, CO 345°C	0.43	86
0.52	Vac 885°C, O_2 495°C, CO 345°C, Vac 685°C	0.40	80
2.1	Vac 885°C, O_2 495°C, CO 495°C	0.17	34

[a] Samples exposed to 200 Torr O_2 for 1 h and then 50 Torr CO for 1.5 h.

[b] H_2 was evolved when H_2O oxidized Cr(II) to Cr(III).

DISCUSSION

Spectroscopic identification of species on Cr/SiO_2. The characterization of the Cr/SiO_2 catalysts was accomplished primarily using infrared spectroscopy with carbon monoxide and nitric oxide as probe molecules. After adsorption of CO on a fully reduced Cr/SiO_2 catalyst, three carbonyl bands at 2192, 2185, and 2182 cm^{-1} were present in the infrared spectrum (Fig. 5) in agreement with the results of Garrone and co-workers (*10–12*). The 2185 cm^{-1} band was strongly pressure dependent, while both the higher and the lower frequency components were more resistant to removal of adsorbed CO. In a previous study of chromium on silica, Zecchina *et al.* (*19*) observed carbonyl bands at about the same wavenumbers as reported here. They assigned these bands to the CO stretching mode of 1 : 1 Cr–CO linear complexes. Garrone and co-workers (*10–12*) have suggested that the frequency difference between the Cr–CO complexes is the result of Cr in different coordination states: Cr_A, coordinated to 2 oxygen atoms, is responsible for the band at 2182 cm^{-1} and Cr_B, coordinated to 3 oxygen atoms, is responsible for the band at 2192 cm^{-1}. The band at 2185 cm^{-1} was attributed to Cr_A ions perturbed by a second CO molecule which is weakly adsorbed.

The dehydration temperature has a dramatic effect on the types of species which are formed. At a dehydration temperature of 885°C, both Cr_A and Cr_B were present, as indicated by the spectra in Fig. 5. At 585°C, Cr_A was present in lower concentrations while the concentration of Cr_B remained essentially constant. These results suggest that the hydroxyl population has a significant effect on the distribution of the Cr(II) species.

An advantage of using NO rather than CO as a probe molecule is derived from the fact that at certain sites dinitrosyl species are formed (*20*) which give rise to pairs of infrared bands (1856 and 1745 cm^{-1} for the sample degassed at 885°C and 1865 and 1744 cm^{-1} for the sample degassed at 585°C). The presence of a dinitrosyl species leads one to conclude that *at least* two coordination sites are available on this type of chromium. In addition, the single band at ca. 1807 cm^{-1} is due to a mononitrosyl, which suggests one available coordination site. Ghiotti *et al.* (*20*), however, have proposed that even this Cr is capable of coordinating a second NO ligand at a sufficiently high pressure.

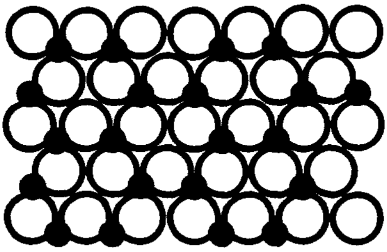
Nature of the active site. The catalytic activity of the Cr/SiO_2 catalyst clearly was favored by more extensive reduction with CO. Even when the catalyst was not completely reduced by CO, the C_2H_6 or the reaction products further reduced the surface. The results of Table 3 indicate that a very large fraction of the chromium on the 0.52 wt% sample may be reduced to Cr(II), for example at 495°C. Thus, the active oxidation state for the dehydrogenation of C_2H_6 is believed to be Cr(II).

Several pieces of evidence suggest the need for a high degree of coordinative unsaturation in the active site. An increase in the initial rate of reaction was observed as the dehydration temperature of the Cr/SiO_2 catalysts was increased from 485 to 815°C. Temperatures greater than 815°C produced a decrease in the initial rate, probably due to a gross change in the surface structure of the catalyst. Over the temperature range from 585 to 885°C the activation energy remained the same, which indicates that the number, but not the type, of sites changed. With a similar Cr/SiO_2 catalyst a maximum activity following dehydroxylation at ca. 900°C has previously been noted for ethylene polymerization (*9*), which is a reaction requiring two or more coordination sites.

The infrared evidence demonstrated that upon increasing the dehydration temperature (a) the number of hydroxyl groups on the silica decreased, (b) the concentration of Cr_A(II) species increased, and (c) the concentration of Cr_B(II) species remained constant. From the infrared spectra of NO presented here and elsewhere (*20*) it is evident that Cr(II) has at least two and perhaps more available coordination sites. The effect of increasing the dehydroxylation temperature may be to increase the number of open coordination sites by removing hydroxyl groups, thereby producing more Cr_A(II), which has at least three available coordination sites (*20*).

The nuclearity of chromium in the active site is also of interest. The data of Fig. 3 show that the catalytic activity increased linearly up to a loading of 0.5 wt% Cr, but at higher loadings the increase was no longer linear. These observations must be interpreted in light of recent work on the state of the surface chromium and the large specific activity of α-chromia. McDaniel (*9*) has recently shown that on Davison 952 silica (280 m^2/g) stabilized Cr(VI) reached a saturation coverage which was an inverse function of the calcination temperature. In McDaniel's experiments the silica was impregnated with CrO_3 to various loadings and then calcined in oxygen, which is a somewhat different treatment than was used for the catalysts reported here. Nevertheless, at a calcination temperature of 870°C he observed that Cr(VI) was stabilized up to an equivalent of 1 wt% Cr, and at higher loadings the CrO_3 was converted to α-Cr_2O_3 as determined by X-ray diffraction.

Based on these results and the data of Fig. 3 we conclude that up to a loading of 0.5% Cr(II) ions of low nuclearity are responsible for the dehydrogenation activity, but at higher loadings both Cr_A(II) ions and reduced chromium ions in an α-Cr_2O_3 phase contribute to the activity. The α-Cr_2O_3 particles tend to become rather large (several hundred Ångstroms) (*9*); therefore, the fraction of surface chromium in this form would be small.



α-Cr_2O_3

α-Chromia has a corundum structure where the open circles represent oxygen atoms and the closed circles represent chromium atoms. One may view the surface as being constructed of ordered pairs of chromium atoms which upon reduction to Cr(II) are responsible for the dehydrogenation activity. It may be stretching the point, however, to conclude that these are sites of low nuclearity. Rather, it seems that the oxidation state and degree of coordinative unsaturation are more important factors than nuclearity in determining catalytic activity for this reaction.

As mentioned earlier, Konig and Tetenyi (*4*) have studied the dehydrogenation of ethane on α-Cr_2O_3, and have proposed coordinatively unsaturated Cr(III) ions as the active sites. They reported initial activities that are an order of magnitude smaller than those observed in this study for α-chromia with the same surface area and at the same reaction conditions. This discrepancy may result from differences in the reducing gas: Konig and Tetenyi used H_2 at 480°C, whereas CO at 495°C was employed in this study. Burwell *et al.* (*21*) have noted that the reduction of *bulk* α-Cr_2O_3 to CrO is difficult at temperatures below 500°C, and it may well be that the low activity of Konig and Tetenyi's sample may have resulted from a lower degree of reduction.

Effect of the support. As can be observed from Table 1, the catalytic activity for ethane dehydrogenation decreased in the order $Cr/Al_2O_3 > Cr/SiO_2 > \alpha\text{-}Cr_2O_3 \gg CrY$. The activities of the Cr/Al_2O_3 and Cr/SiO_2 catalysts were surprisingly similar, which suggests that the active sites are essentially the same. Therefore, the support must not have a significant electronic effect on the chromium.

Ashmawy (2) has studied the dehydrogenation of ethane on Cr/Al_2O_3 and concluded that both Cr(II) and Cr(III) are active, although Cr(II) seemed to be the most active ion. Again, Cr(III) initially present on the catalyst may have been reduced to Cr(II) by contact with ethane at 500°C.

Van Reijen *et al.* (*1*) have explored the dehydrogenation of cyclohexane over Cr/SiO_2 and Cr/Al_2O_3 catalysts and have reported an activation energy of 26 kcal/mole. The reaction was first order in cyclohexane. These authors also noted poisoning effects of H_2O which they attributed to the oxidation of Cr(II) to Cr(III) according to reaction (1). The activity was attributed to Cr(II) in a state of low coordination.

Wittgen *et al.* (*22*) concluded that the hydrogenation of propylene over Cr/SiO_2 occurred on Cr(III) ions in a state of low coordination. Their conclusion, however, was based largely on the effect of H_2 in deactivating the catalyst, presumably by reducing chromium to Cr(II). This interpretation is not straightforward since reduction by H_2 results in the formation of H_2O, which promotes the formation of Cr_2O_3. Because of this complicating role of H_2O most investigators employ CO, rather than H_2, as a reducing gas when working with chromium.

When Cr(III)Y zeolite was used as the catalyst, negligible activity (Table 1) was observed for the dehydrogenation of ethane at 495°C in the recirculating reactor. Based upon our model for the active site the inactivity of Cr(III)Y could result from a failure to reduce the Cr(III) to Cr(II) or from inaccessible Cr ions. Only $[Cr^{III}(NO)_2]^{3+}$ complexes were observed by infrared spectroscopy, which is consistent with the fact that Cr(III) in zeolite-Y is very difficult to reduce to Cr(II) (*17*). From X-ray diffraction experiments, Pearce and Mortier (*23*) have shown that the Cr(III) cations in the dehydrated CrY reside primarily at site I′; however, in order to form stable nitrosyl complexes upon NO addition, these cations migrate to accessible sites in the large cages (site II). Because of thermal disorder it is expected that at least part of the Cr ions would be available to interact with ethane at 495°C. In a separate experiment La^{3+} ions were exchanged into a Y-zeolite before ion-exchange with Cr ions, in order to force the Cr(III) ions to occupy sites near the supercage. This sample, likewise, did not exhibit any activity for ethane dehydrogenation. The accessibility of Cr ions is also demonstrated by the activity which these zeolites exhibit for the polymerization of ethylene at 50°C (*24*). The evidence suggests, therefore, that the difficulty in reducing Cr(III) to Cr(II), rather than the lack of accessibility of Cr ions, is responsible for the inactivity of the CrY zeolites.

CONCLUSIONS

Reduced chromium ions on a well dehydroxylated silica are active for the selective dehydrogenation of ethane to ethylene, although the catalyst is rapidly poisoned by coking. At low loadings the active site is believed to be a coordinatively unsaturated Cr(II) ion, which is in a state of low nuclearity. The nuclearity may not be an important factor, however, as indicated by the observation that the specific activity of α-Cr_2O_3 was about the same as that of Cr/SiO_2 and Cr/Al_2O_3.

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