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Reduction and Aromatization Activity of Chromia–Alumina Catalysts

II. An XPS Investigation of Chromia–Alumina Catalysts

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Chromia–alumina catalysts with 1.8 to 20 wt% Cr_2O_3, including samples containing additional elements as K, Pt, and Re, were reduced in H_2 in the 773–923 K temperature range at atmospheric pressure and investigated by X-ray photoelectron spectroscopy. In the Cr 2*p* spectra of oxidized samples, Cr^{6+} and Cr^{3+} were detected. While Cr^{6-} was rapidly transformed to Cr^{3+} in the initial reduction phase a new chromium signal emerged after longer exposure times. This signal representing the product of Cr^{3+} reduction was ascribed to highly dispersed zerovalent chromium with metallic band structure not formed, subject to a stabilization by the support. Signals that could be attributed to Cr^{2+} and Cr^{5+} were not found in this study. With regard to catalytic experiments reported earlier, the aromatization activity of chromia–alumina catalysts was ascribed to Cr^{3+} coordinatively unsaturated sites.

INTRODUCTION

In Part I of this paper (*1*), it was confirmed that the reduction of oxidized chromia–alumina catalysts at 773–923 K with H_2 does not stop at the Cr(III) state but continues slowly forming chromium species of unknown identity. These species, which would be assumed to be Cr^{2+} according to the literature (*2*), are not responsible for the aromatization activity exhibited by these catalysts. The reduction of Cr(III) was delayed but not entirely suppressed by a water content of the reducing gas in the order of 1 vol%. The identification—whenever possible—of chromium valence states obtained by the methods used in Part I was not unambiguous.

In view of the high efficiency of photoelectron spectroscopy (XPS) in the characterization of surface species in heterogeneous catalysts (*3*) the elucidation of this problem was expected from an XPS study of catalysts containing Cr_2O_3 on Al_2O_3. The reduction of these catalysts was investigated in the temperature range of 773–923 K varying the chromia content of the samples. Pt-containing systems relevant to catalytic reforming were included as the formation of zerovalent chromium has been postulated for these catalysts on the basis of indirect evidence (disappearance of DRS lines (*4*), XRD of reduced CrO_3/H_2PtCl_6 mixtures (*5*)).

Chromium-based catalysts as well as pure chromium–oxygen compounds have been repeatedly studied by XPS (Al_2O_3 carrier (*6–8*), SiO_2 carrier (*9–12*), pure compounds, e.g. (*13, 14*)). However, evidence concerning species other than Cr^{3+} and Cr^{6+} is conflicting; in particular, no valence state lower than +3 has been detected on the Al_2O_3 carrier. This may be due to the mild reduction conditions applied (*6*) and air contact during the transfer of samples to the spectrometer (*8*). On the silica carrier, Cr^{2+} was indicated by Best *et al.* (*10*) and well established by Merryfield *et al.* (*11*) and Strutz (*12*), confirming the tempting parallelism that inspires interpretation of the generally indirect evidence for low-valent chromium on Al_2O_3 in favor of Cr^{2+}.

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EXPERIMENTAL

1. Materials

Chromia/alumina catalysts containing 2.3, 7.8, and 20 wt% Cr_2O_3 (the latter with 4 wt% K_2O) were those described in (*1*) (catalysts Cr2.3, Cr7.8, and Cr20K4, resp.). They were calcined in air at 823 K for 2 h prior to use.

Additionally, two catalysts containing platinum were used (Cr1.8PtRe: 1.8% Cr_2O_3, 2% Pt, 1.35% Re; Cr1.8Pt: 1.8% Cr_2O_3, 0.62% Pt). They were prepared by sequential impregnation of γ-Al_2O_3 with H_2PtCl_6, chromic anhydride, and ammonium perrhenate. After a 2-h calcination at 773 K, they were reduced in flowing H_2 by increasing the temperature from ambient to 773 K in the course of 1 h. Part of each catalyst was kept under these conditions for another hour, the rest was exposed to an *n*-hexane/H_2 mixture ($\approx$1:6; 6 liters/h) at the same temperature for 1 h. After these treatments the catalysts were stored in air. They will be referred to as "without coke" and "coked," respectively. H_2 and Ar were deoxygenated over MnO/Al_2O_3 and dried over $Mg(ClO_4)_2$ (residual concentrations of $<10^{-3}$ ppm O_2 and <1 ppm H_2O (*15, 16*)) immediately before entering the pretreatment reactor mentioned below.

2. XPS Apparatus and Procedure

An AEI ES 200B spectrometer with Al$K\alpha$ excitation (1486.6 eV) was used. Spectra were recorded at a pressure of $0.5–1 \times 10^{-7}$ Torr, running the X-ray source at 12 kV and 16 mA. The Cr $2p$ spectra were accumulated with a MCA "Nicolet" and then transferred to the PDP 11/03L computer incorporated in the XSAM 800 spectrometer of Kratos Ltd. for spectrum deconvolution. Binding energies were referred to C $1s$ = 285.0 eV. As severe reduction may lead to a distortion of the C $1s$ peak data referred to Al $2p$ = 75.1 eV, the mean value for Al $2p$ in nonreduced samples, are also given. The difference is at most 0.3 eV. The overall charging of our (insulating) samples was in the range of 4.5–5 eV.

The reduction of the samples was performed in a special pretreatment reactor, which was supplied with a transfer lock designed for the transfer of samples in a protective gas atmosphere. This sample transfer system, which permitted the transfer of pyrophoric samples (W metal powder) without any trace of reoxidation, will be described in more detail elsewhere. In a typical experiment, calcined or prereduced catalysts were crushed, pressed into loops of nickel wire, and mounted on the sample probe, which was inserted into the pretreatment reactor. The sample was heated to the desired temperature in Ar (or H_2 for Pt-containing catalysts), reduced in 6 liters/h H_2 and subsequently cooled down in Ar. The process of attaching the transfer system to the fast insertion lock of the spectrometer is arranged in a way that precludes the atmosphere from the interior of the system at normal performance. Traces of oxygen that may have possibly penetrated are confined to the transfer lock volume by two Ar flows from the reactor and from the fast insertion lock of the spectrometer meeting in this unit and being discharged from here. Thus, after attaching the sample transfer system to the spectrometer, the transfer lock volume was thoroughly flushed with Ar before the sample probe was moved forward to enter the fast insertion lock of the spectrometer.

The deconvolution of Cr $2p$ spectra was accomplished with a standard peak synthesis program, in which spectra are synthesized from arbitrary Gaussian singlet lines. Constraints providing physical consistency are introduced by the user. In particular, this applies to linewidths and intensity ratios of doublets and of lines with adjacent satellites. In our case, the Cr $2p^{1/2}$/Cr $2p^{3/2}$ intensity ratio was kept in the limits of 0.40 ± 0.03 (*6*) for Cr(VI), and 0.55 ± 0.03 (*17*) for all other chromium species.

The satellite structure of Cr(III) was studied with samples showing the spectrum of Cr(III) only (short reduction at 773 K, contact with air), with special attention to the region between Cr $2p^{1/2}$ and Cr $2p^{3/2}$. As a consequence, the distance and the intensity ratio between the Cr $2p^{3/2}$ satellite and the main line were kept in the limits of 4.1 ± 0.1 eV and 0.32 ± 0.03 for all spectra. The treatment of the Cr $2p^{1/2}$ satellite, not essential for the results to be discussed, was less stringent. No satellites were assumed for chromium species other than Cr^{3+}.

Binding energies (b.e.) were determined with an accuracy of 0.2 eV, spacing between lines with 0.1 eV. Exceptions resulting from minor concentrations of the particular species are indicated by brackets.

RESULTS

Examples of Cr $2p$ spectra are shown in Figs. 1 and 2, with the individual doublets resulting from deconvolution inserted. Relevant data are summarized and compared with the literature in Tables 1 and 2.

The spectra of the oxidized samples (example Cr20K4—Fig. 1, curve a) were readily decomposed into two doublets with b.e. and (with the exception of Cr 2.3) spin-orbit splitting characteristic of Cr^{6+} and Cr^{3+} (Table 1). A nonlinear background as revealed by an extended scan in the case of Cr2.3 is, obviously, responsible for the remaining small inconsistencies centered at 583–584 eV (2–3% of total area in Cr7.8, 9% in Cr2.3). A third doublet indicative of Cr^{n+} ($n = 4, 5$) was not needed to synthesize the spectra of the oxidized samples.

Extensive photoreduction of Cr^{6+} was found on repeating scans with the Cr20K4 sample. Correction was not made, however, for conversion data of Table 1, in which higher values would be expected in particular for Cr2.3 and Cr7.8 because of longer exposure times. Photoreduction of Cr^{3+} was not observed.

Cr^{6+} was entirely removed by a 10-min H_2 reduction at 773 K, leaving the Cr^{3+} signal only (Cr20K4—Fig. 1, curve b). When the catalyst was reduced at 823 or 923 K for 2 h, a new line appeared (Figs. 1c and d), with a b.e. well below that of metallic chromium (574.0 eV). This line turned out to be the $2p^{3/2}$ compound of a doublet present in all investigated catalysts after appropriate reduction procedures (Table 2; examples in Fig. 2). In the absence of Pt the b.e. of the

TABLE 1

Binding Energies, Spin-Orbit Splitting (in eV), Reduction Extent, and Intensity Ratio between Cr $2p$ and Al $2p$ in oxidized samples (Compared with Literature Data) C $1s$ = 285.0 eV[a]

Catalyst	Cr(III)		Cr(VI)		A[b]	$\frac{I_{\mathrm{Cr}\ 2p}}{I_{\mathrm{Al}\ 2p}}$
	E_B	$\Delta E_{s.o.}$	E_B	$\Delta E_{s.o.}$		
Cr20K4	577.4	9.7	580.1	9.2	0.37	1.25
Cr7.8	577.3	9.5	579.9	9.1	0.20	0.51
Cr2.3	577.4	9.2	580.4	9.1	0.25	0.23
Cr_2O_3/Al_2O_3	577.2	9.8(*6*)	580.6	9.1(*6*)	—	—
	577.6	9.8(*8*)	579.7	9.2(*8*)	—	—
CrO_3	—	—	579.1	9.1(*11*)	—	—
	—	—	580.3	9.1(*8*)	—	—

[a] Al $2p$ = 75.1 ± 0.1 eV.

[b] $A = \frac{I_{\mathrm{Cr(VI)}}}{I_{\mathrm{Cr(VI)}} + I_{\mathrm{Cr(III)}}}$; not corrected for photoreduction.

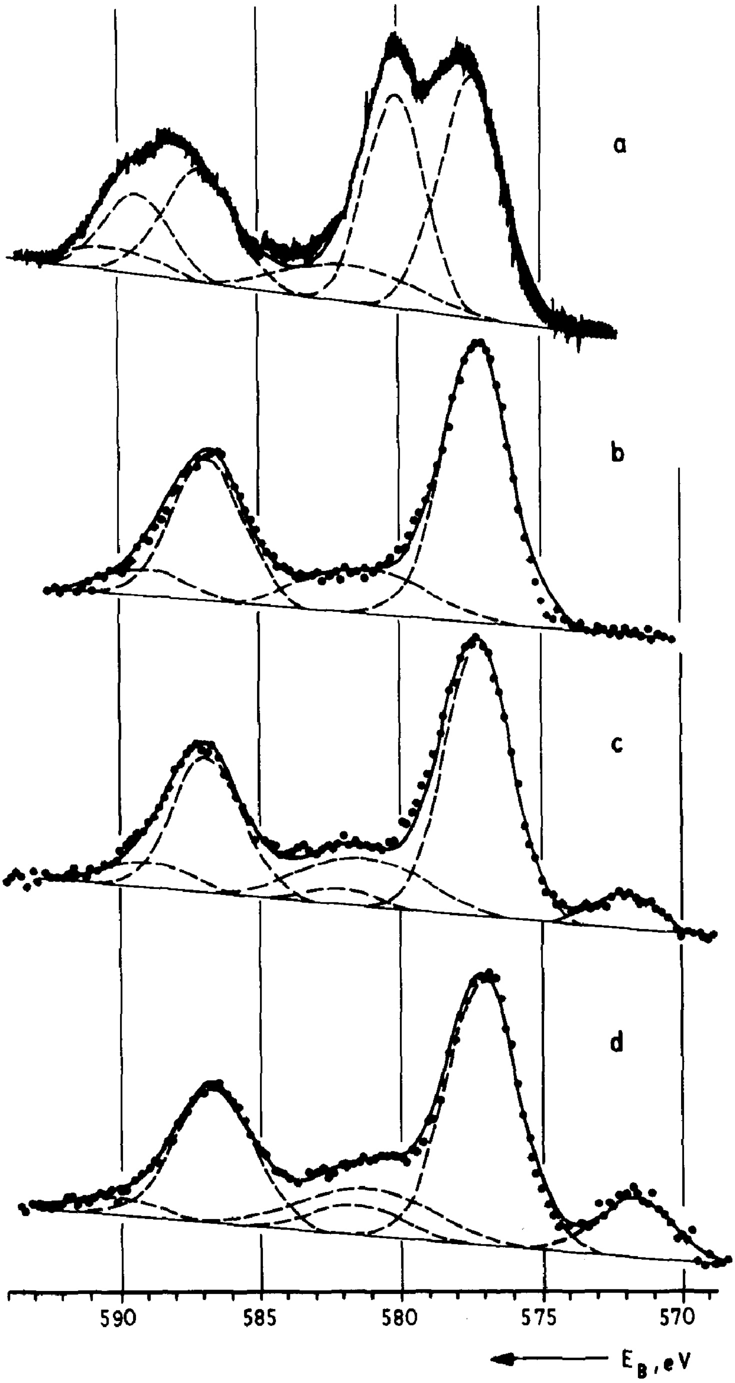

FIG. 1. Cr 2*p* spectra of Cr20K4 after different pretreatments (deconvolution inserted). (a) Oxidized 2 h at 823 K (after previous reduction); (b) pretreatment (a) + 10 min reduction at 773 K; (c) pretreatment (a) + 2 h reduction at 823 K; (d) pretreatment (a) + 2 h reduction at 923 K.

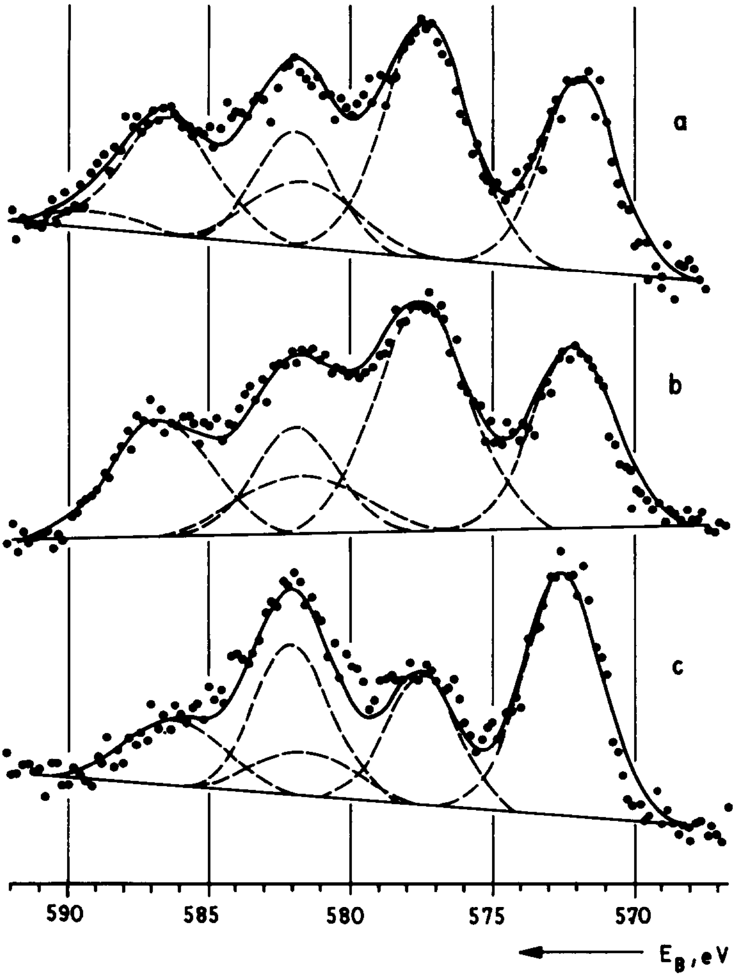

FIG. 2. Cr 2*p* spectra of samples with high reduction extent (deconvolution inserted). (a) Cr2.3, reduced 2 h at 823 K, (b) Cr1.8 Pt, reduced 1 h at 773 K, (c) Cr1.8 Pt, coked, reduced 1 h at 773 K.

new $2p^{3/2}$ line was 571.7–572.0 eV (with an exception of Cr7.8 R823) exhibiting a slight tendency to lower values at higher reduction temperatures. In the presence of Pt the new line became the main component of the spectrum (coked samples), with a slight shift to higher b.e. (0.4–0.7 eV). The spin-orbit splitting of the new doublet was 9.8–10.1 eV, with slightly lower values for the coked Pt-containing samples.

The new doublet, characteristic data of which substantially deviate from data available for Cr^{2+} (*11, 12*), is markedly different from the signal of bulk chromium metal as well. We assign it tentatively to Cr(0)/Al_2O_3, assuming a strong influence of the carrier on the Cr(0) species.

In the absence of platinum, the contribution of the Cr(0) signal to the overall intensity of the Cr 2*p* spectrum, being a rough measure of the reduction extent, decreased with growing chromia content and increased with temperature, possibly with asymptotic behavior in the case of the Cr2.3 sample. With the platinum-containing samples reduction extents as high as 67% were observed. Carbon deposits obviously take part in the reduction: C 1*s* peaks of coked

TABLE 2

Binding Energies, Spin-Orbit Splitting (in eV), Reduction Extent, and Intensity Ratio between Cr 2*p* and Al 2*p* in Reduced Samples (Compared with Literature Data) C 1*s* = 285.0 eV[a]

Catalyst	Treatment[b]	Cr(III)		Cr(0)		$\frac{I_{Cr(0)}}{I_{Cr(III)} + I_{Cr(0)}}$	$\frac{I_{Cr\ 2p}}{I_{Al\ 2p}}$	
		E_B	$\Delta E_{s.o.}$	E_B	$\Delta E_{s.o.}$			
Cr20K4	773/10	577.3 (577.5)	9.6	—	—	—	1.41	
	823/120	577.2 (577.4)	9.6	572.0 (572.2)	[10.2]	0.08	1.44	
	923/120	577.1 (577.4)	9.6	571.7 (572.0)	9.9	0.15	1.55	
Cr7.8	823/120	577.6	9.7	572.6	10.1	0.17	1.00	
	923/120	577.6	9.4	571.9	9.9	0.22	0.84	
Cr2.3	823/120	577.4 (577.1)	9.1	572.0 (571.7)	10.0	0.34	0.51	
	923/120	577.6 (577.3)	9.2	571.8 (571.5)	9.8	0.38	0.49	
Cr1.8PtRe	773/60	577.5 (577.3)	9.1	572.1 (571.9)	9.8	0.27	0.34	
" , coked	773/60	577.4	9.2	572.8	9.7	0.52	0.43	
Cr1.8Pt	773/60	577.5	9.2	572.1	9.8	0.38	0.20	
" , coked	773/60	577.5	[8.8]	572.5	9.6	0.67	0.32	
Cr (metal)				574.1				
Cr_2O_3/Cr(metal)		576.2	9.8(*13*)	574.4	9.3 (*13*)	Cr^{n+}	E_B	$\Delta E_{s.o.}$
		576.6	9.8(*8*)	574.0	9.0 (*14*)			
Cr_2O_3/Al_2O_3		577.2	9.8(*6*)	—	—	$n = 5$	579.4	9.1 (*6*)
		577.6	9.8(*8*)	—	—		577.8	9.1 (*8*)
Cr_2O_3/SiO_2		577.6	9.5^c(*11*)	—	—	$n = 2$	576.6	9.6 (*11*)
		577.1	10.0^c(*10*)	—	—		577.1	(*12*)
							577.9	

[a] b.e. referred to Al 2*p* = 75.1 eV added in parntheses if divergence exceeds 0.1 eV.

[b] *Temperature in K; time in min.*

[c] 1.1% Cr/SiO_2 in (*11*), 8% Cr/SiO_2 in (*10*).

samples were found to be only slightly higher after reduction than those of samples without coke (e.g., I_{C1s}/I_{Al2p} for Cr1.8PtRe: coked 0.16; without coke 0.12), while the reduction extent was significantly increased. A similar enhancement of reduction was not observed in the absence of Pt.

The $2p^{3/2}$ line of Cr^{3+} was found at 577.1–577.6 eV. Remarkably, spin-orbit splitting depended on chromia content both in reduced and oxidized samples. While the 9.4–9.7 eV measured for Cr20K4 and Cr7.8 are within the range expected for Cr^{3+}, spin-orbit splittings of 9.1–9.3 eV for Cr2.3 and Pt-containing samples are unexpected and make this doublet resemble the Cr(V) signal reported by Okamoto *et al.* (*6*) (see Table 2).

The Cr 2*p*/Al 2*p* intensity ratio of Cr_2O_3/Al_2O_3 catalysts is markedly increased after reduction, in particular at lower chromia content. The variation of this intensity ratio with increasing temperature is not very pronounced, the trends being suspected to be within the range of experimental error. This is confirmed by the K 2*p*/Al 2*p* intensity ratio reported in Table 3, where the intensity step between oxidized and reduced samples is significant while no unambiguous trend can be detected among the reduced catalysts.

Reduction affects also the b.e. of the K 2*p* line, which is shifted from 293.5 eV in the oxidized sample to 293.9–294.1 eV in the reduced ones.

TABLE 3

Influence of H_2 Reduction on the K 2*p* Line of the Cr20K4 Sample

Pretreatment	E_B (K $2p^{2/3}$)^a (eV)	$\frac{I_{K\ 2p}}{I_{Al\ 2p}}$
Ox	293.5	0.31
R773/10	293.9	0.56
R823/120	294.1	0.51
R923/120	294.1	0.58

^{a} Referred to Al 2*p* = 75.1 eV.

DISCUSSION

1. *Identification of New Lines*

Cr(0). Though differences between the spectrum of metallic chromium and the new doublet with Cr $2p^{3/2}$ = 571.7–572.0 eV are substantial in respect of binding energy and spin-orbit splitting, there is no doubt that the new doublet originates from a zerovalent chromium species.

Some information about the state of this species is obtained from the Cr 2*p* spin-orbit splitting ($\Delta E_{s.o.}$) reflecting exchange interactions between 2*p* and unpaired 3*d* electrons (*6*). Thus, $\Delta E_{s.o.}$ is at a maximum at Cr^{3+} (three unpaired 3*d* electrons) and a minimum at Cr^{6+} (no unpaired 3*d* electrons) and metallic chromium (delocalization of 3*d* electrons in the metallic bond). In terms of this model, the markedly higher spin-orbit splitting of Cr(0)/Al_2O_3 compared to the bulk metal reflects the absence of the metallic band structure, i.e., a very high, possibly atomic dispersion of Cr(0). The increased reducibility of catalysts with low chromia content supports this conclusion. It is, moreover, in accordance with ESR studies on reduced Cr_2O_3/Al_2O_3 catalysts indicating (along with a decrease and broadening of the β-signal, which is attributed to dehydroxylation (*18*)) a decrease or even disappearance of the δ-signal (*17, 20*) generally ascribed to isolated Cr^{3+} ions located on or below the Al_2O_3 surface.

The interpretation of the unusually high negative shift between the binding energies of chromium metal and Cr(0)/Al_2O_3, which is in contrast to many examples of noble metals on oxidic supports as given, e.g., in (*5*), is somewhat speculative at the present level of knowledge. An influence of overall charging is unlikely: the amount of overall charging was the same as in the oxidized samples and no unusual shifts, peak broadening, or distortions were found with the other lines (Al 2*p*, C 1*s*, O 1*s*, K 2*p*, Re 4*f*). A contribution of local charging on the metal particles cannot be ruled out but would not alone be sufficient to describe the state of Cr(0)/Al_2O_3, the anomalous spin-orbit splitting of which cannot originate from a charging effect. Moreover, it would remain unclear why local charging occurs with Cr(0)/Al_2O_3 but not with noble metals supported on various oxidic carriers.

More likely, the observed shifts originate from electronic and relaxation effects due to a strong interaction between the highly dispersed Cr(0) and the alumina carrier and increasing the electron density at the chromium atoms or improving the screening of the vacancy in the final state. By analogy with the alloy model of strong metal–support interaction (SMSI) suggested by den Otter and Dautzenberg (*21*) and Kunimori *et al.* (*22*) for Pt/Al_2O_3, a local reduction of the Al_2O_3 around the chromium particles and the formation of small Al–Cr clusters may be assumed.

In these clusters, charge transfer from aluminum to chromium in the initial or final state would cause the negative shift of the Cr 2*p* binding energy, the magnitude of which should be strongly dependent on the number of Cr atoms participant in the cluster and hence, at a maximum for the highly dispersed chromium on these catalysts. Interaction with other metals present, e.g., Pt, may give rise to further minor modifications as observed in the case of the coked Pt-containing samples.

Unfortunately, all these conclusions must be drawn from the Cr 2*p* spectra alone; complementary evidence is not yet available. There was not observed any substantial change of the Al 2*p* signal on reduction. However, at the given concentrations of zerovalent chromium (max. 2—2.5%, related to (Cr + Al)), the detection of a peak due to a reduced form of Al adjacent to the intense Al^{3+} signal should be difficult anyway. The literature on bulk Cr–Al alloys is complex, with charge transfer in both directions claimed (*23*). Considerable negative shifts of metallic core levels due to electronic interactions have been observed for Cu in contact with Pt (*24*) and polystyrene (*25*) (−1−−1.5 eV), for Pd on La_2O_3 (*26*) and, in our own work, for W(0) and Mo(0) on Al_2O_3 (−0.5−−1.3 eV) (*27*).

The reduction of Cr(III) to Cr(0) in the thoroughly purified gases applied here is not seriously contested by thermodynamics ($\approx$0.5 ppm H_2O permissible at 823 K as estimated from bulk-phase thermodynamic data (*28*); a high degree of Cr(III) dispersion may favor its reduction). On the other hand, the observation made in (*1*) that reduction may proceed in H_2 containing 0.3–0.4 vol% H_2O already at 773 K implies the existence of a stabilization of zerovalent chromium by the support or, if present, by Pt. The strong interaction with reduced spots of the support mentioned above may exert a stabilizing effect. However, additional effort is required to elucidate the detailed mechanism of Cr(0) stabilization.

Cr(III). Okamoto *et al.* (*6*) were the first to find that the spin-orbit splitting of the Cr 2*p* doublet emerging on mild reduction of oxidized Cr_2O_3/Al_2O_3 catalysts depends on the chromia content of the catalyst, while the binding energy remains nearly constant. The doublet with $\Delta E_{s.o.}$ = 9.0–9.2 eV found at low chromia content was attributed by them to Cr^{5+}. It was not observed, however, after a very long reduction time (10 h), or when the catalyst had been previously calcined in air at 1173 K, where the signal typical of Cr^{3+} was found instead.

The dependence of the Cr(III) signal in our spectra on the Cr_2O_3 concentration is quite similar. We would not, however, expect the existence of Cr^{5+} after the reduction procedures applied (e.g., 973 K, 2 h) and ascribe the doublet with low $\Delta E_{s.o.}$ to highly dispersed Cr^{3+}, probably involved in an interaction with the carrier (e.g., via Lewis acid centers of Al_2O_3), dispersion of the chromium ions rather than their oxidation state being the property reflected in the shift of $\Delta E_{s.o.}$. A similar dependence of $\Delta E_{s.o.}$ for the Cr(III) doublet on chromia concentration is revealed for the SiO_2 carrier by a comparison of data given in (*10*, *11*) (which should be justified for energy differences, neglecting absolute values): $\Delta E_{s.o.}$ was found to be 10.0 eV at 8% Cr/SiO_2, and 9.5 eV at 1.1% Cr/SiO_2 (Table 2). Recently, the same tendency has been observed for Cr(III) in CrY zeolites by Wichterlová *et. al.* (*29*).

2. *Surface Chemistry of the Cr_2O_3/Al_2O_3 System*

The trends of Cr(0) formation presented in Table 2 coincide with the reduction tendencies given in the literature (*2, 30*) (where Cr^{2+} formation is assumed) and confirmed in the preceding paper (*1*). Agreement, in particular with (*1*), covers the order of reduction extent as well, whereas some quantitative deviations toward higher reduction degrees in the case of the XPS-analyzed samples are plausible in view of differences in reduction conditions and performance and analytic methods. It may be concluded, therefore, that the product of slow-stage reduction of Cr_2O_3/Al_2O_3 catalysts is not Cr^{2+}, but Cr(0)/Al_2O_3. This species is, however, not responsible for the aromatization activity of these catalysts, as shown in (*1*).

Zerovalent chromium is also present in the platinum-containing catalysts as anticipated by Kozlov (*3*). An interaction between the chromium and platinum, which was found by Engels *et al.* (*4*) for reduced CrO_3–H_2PtCl_6 mixtures, seems to occur on the Al_2O_3 carrier as well, if the extent of Cr(III) reduction is high enough. A catalytic influence of Pt on Cr(III) reduction is likely but not yet unambiguously established. The reduction of Cr(III) by carbon is obviously catalyzed by Pt, in agreement with observations made by Ott and Raub for bulk substances in the 1100–1300 K region (*31*). In view of these observations and regarding trends of reducibility with chromia content, high Cr(III) reduction extents may be expected in Pt–Cr and Pt–Re–Cr–Al_2O_3 systems of commercial interest (*32*).

The existence of Cr^{2+}/Al_2O_3 under the conditions employed remains questionable after this study. There was not found any indication of a line between Cr(III) and Cr(0)/Al_2O_3, e.g., at ≈1 eV distance from Cr(III) like the Cr(II) signals on SiO_2 (*11*) and in CrY (*29*). Of course, spectroscopic evidence can hardly result in the complete exclusion of a species; however, coincidence should be noted between our conclusions and results of Przhevalskaya *et al.*, who found by ESR that Cr(II) compounds adsorbed on Al_2O_3 were oxidized to Cr(III) on mere evacuation at 773 K, probably by surface hydroxyl groups (*33*).

The catalytic relevance of hypothetic Cr^{2+} species in the catalysts investigated is questioned by a further argument anticipated in (*1*). The aromatization activity of the previously oxidized Cr20K4 catalyst was stable after an instantaneous reduction process the product of which is confirmed to be Cr^{3+}. If traces of Cr^{2+} possibly coexisting with the Cr^{3+} determined aromatization activity they would have to emerge in this instantaneous reduction and undergo no modification at further H_2 treatment to explain the activity behavior observed in (*1*).

The conclusions about the irrelevance of Cr^{2+} on Al_2O_3 seem to be in disagreement with the formation and the low-temperature hydrogenation activity of Cr^{2+} fixed to Al_2O_3 via allyl complexes, as stated by Iwasawa (*34*). It should, however, be noted that the reference impregnation catalyst used in (*34*) showed its maximum activity at a medium oxidation number of ≈3 and was deactivated by further reduction. The unusual redox properties of the fixed Cr catalysts disappeared after some redox cycles. Their origin certainly needs further elucidation.

Cr^{5+}/Al_2O_3 is another species, for which no evidence was found in our study although its presence at least in the oxidized samples would be expected according to ESR studies of the literature (*19, 20*). The XPS evidence for this species (*6, 8*) widely discussed in the literature on the basis of ESR data seems to be not indisputable, and further effort for its reliable photoelectron spectroscopic characterization is needed.

3. Surface Modification during Rapid-Stage reduction

The intensity ratios $I_{\mathrm{Cr}\,2p}/I_{\mathrm{Al}\,2p}$ (Tables 1 and 2) indicate that the reduction of surface Cr^{6+} in the oxidized catalyst involves a redispersion of chromia, probably induced by the instanteneous heat production near the surface (*1*). The increase is less pronounced in the case of Cr20K4, as the chromia coverage is considerable in this catalyst anyway resulting, for instance, in pore blocking phenomena (*35*). Surface alteration is well reflected in this case in the substantial increase of the K 2*p*/Al 2*p* intensity ratio (Table 3), which is accompanied by a slight shift of the K 2*p* line. Obviously, K^+ ions covered in the oxidized form become "visible" after reduction. The binding energy shift of K 2*p* is ascribed to a migration of the K^+ ion from chromate ions to the alumina on reduction in agreement with early results of Rozengart *et al.* (*36*) who reported the formation of extractable potassium aluminate after a 3-min reduction of oxidized $Cr_2O_3/K_2O/Al_2O_3$ catalysts.

Redispersion simultaneous with rapid-stage reduction gives a plausible interpretation to the difference in slow-stage reduction extent observed in TPR of fresh and stabilized catalysts (*1*). The high Cr^{6+} content of fresh samples would imply a more intense redispersion resulting in higher reducibility of the Cr^{3+} formed. Similarly, reduction started at the very reduction temperature as in the pretreatment reactor used in this study would render a higher Cr^{3+} dispersion and, hence, a higher slow-stage reduction extent than the milder TPR regime.

CONCLUSIONS

The slow reduction process observed with Cr_2O_3/Al_2O_3 catalysts was found to be a conversion of highly disperse fractions of chromia to zerovalent chromium species stabilized probably by a strong interaction with the carrier. Formation of Cr^{2+} was not observed on the Al_2O_3 carrier.

The aromatization activity was ascribed to Cr^{3+} coordinatively unsaturated sites. When starting from oxidized samples the active surface is formed in an instantaneous reduction of Cr^{6+} accompanied by a redispersion of chromia on the carrier.

REFERENCES

1. Grünert, W., Saffert, W., Feldhaus, R., and Anders, K., *J. Catal.*, **98,** 1986.

2. Sloveckaya, K. I., Alyoshin, E. G., and Rubinshtein A. M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 749 (1973).

3. Kozlov, N. S., Skrigan, E. A., Senkov, G. M., Dmitrieva, L. P., Kupcha, A., and Gorbachevich, M. F., *Kinet. Catal.* **21,** 1023 (1980).

4. Engels, S., Lausch, H., Mahlow, P., Anders, K., Feldhaus, R., Vieweg, H.-G., Peplinski, B., Wilde, M., and Kraak, P., *Chem. Tech. (Leipzig)* **37,** 157 (1985).

5. Minachev, Kh. M., Antoshin, G. V., and Shpiro, E. S., "Fotoelektronnaya spektroskopiya i eyo primeneniye v katalize" (Photoelectron Spectroscopy and Its Application in Catalysis). Nauka, Moscow, 1981.

6. Okamoto, Y., Fujii, M., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* **49,** 859 (1976).

7. Minachev, Kh. M., Khodakov, Yu. S., Antoshin, S. V., Zasypkin, V. V., Shpiro, E. S., and Shchibrya, G. G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 549 (1981).

8. Jagannathan, K., Srinivasan, A., and Rao, C. N. R., *J. Catal.* **69,** 418 (1981).

9. Cimino, A., de Angelis, B. A., Luchetti, A., and Minelli, O., *J. Catal.* **45,** 316 (1976).

10. Best, S. S., Squires, R. G., and Walton, R. A., *J. Catal.* **47,** 292 (1977).

11. Merryfield, R., McDaniel, M., and Parks, G., *J. Catal.* **77,** 348 (1982).

12. Strutz, J., thesis. Berlin (West), 1979.

13. Allen, G. C., Curtis, M. T., Hooper, A. J., and Tucker, P. M., *J. Chem. Soc., Dalton Trans.*, 1675 (1973).

14. Allen, G. C., Tucker, P. M., and Wild, R. K., *J. Chem. Soc., Faraday Trans. 2* **74,** 1126 (1978).

15. McIlwrick, C. R., and Phillips, C. S. G., *J. Phys. E.: Sci. Instrum.* **6,** 1208 (1973).

16. Lux, H., "Anorganisch-chemische Experimentierkunst" (The Art of Anorganic Chemical Experiment), p. 350. Leipzig, 1970.

17. Scofield, J. H., *J. Electron Spectrosc. Relat. Phenom.* **8,** 129 (1976).

18. Kazanski, V. B., *Kinet. Catal.* **8,** 1125 (1967).
19. Segawa, K. I., Ishii, H., and Ueda, H., *Sekiyu Gakkaishi* **22,** (2), 84 (1979).
20. Ashmawy, F., *J. Chem. Soc., Faraday Trans.* 1 **76,** 2096 (1980).
21. den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53,** 116 (1978).
22. Kunimori, K., Okouchi, T., and Uchijima, T., *Chem. Lett.,* 1513 (1980).
23. Lawniczniak-Jabłonska, K., Minni, E. E., Pelka, J., Suominen, E., and Auleytner, J., *Phys. Status Solidi B* **123,** 627 (1984); Wenger, A., and Steineman, S., *Helv. Phys. Acta.* **47,** 321 (1974); Köster, W., and Wachtal, K., and Grube, K., *Z. Metallk.* **54,** 393 (1963).
24. Hammond, J. S., and Winograd, N., *J. Electroanal. Chem. Interfacial Electrochem.* **80,** 123 (1977).
25. Burkstrand, J. M., *Surf. Sci.* **78,** 513 (1978).
26. Fleisch, T. H., Hicks, R. F., and Bell, A. T., *J. Catal.* **87,** 398 (1984).
27. Grünert, W., and Shpiro, E. S., unpublished results.
28. Chu, W. F., and Rahmel, A., *Metall. Trans. B* **10B,** 401 (1979).
29. Wichterlová, B., Krajciková, L., Tvaruzkova, Z., and Beran, S., *J. Chem. Soc., Faraday Trans. 1* **80,** 2639 (1984).
30. Sloveckaya, K. I., Rubinstein, A. M., Timofeyeva, E. A., Alyoshin, E. G., and Ivankovski, V. E., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1476 (1975).
31. Ott, D., and Raub, C. J., *Platinum Met. Rev.* **20** (3), 79 (1976).
32. Anders, K., *et al.,* DD 142271 (21 Mar 1978).
33. Przhevalskaya, L. K., Shvec, V. A., and Kazanski, V. B., *Kinet. Catal.* **20,** 1005 (1979).
34. Iwasawa, Y., *J. Mol. Catal.* **17,** 93 (1982).
35. Bremer, H., Muche, J., and Wilde, M., *Z. Anorg. Allg. Chem.* **407,** 40, 51 (1974).
36. Rozengart, M. I., Kuznecova, Z. F., and Gitis, K. M., *Neftekhimiya* **5,** 17 (1965).