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Preparation and Characterization of Al_2O_3-Attached Cr(II) Dimer and Cr(II) Monolayer Catalysts

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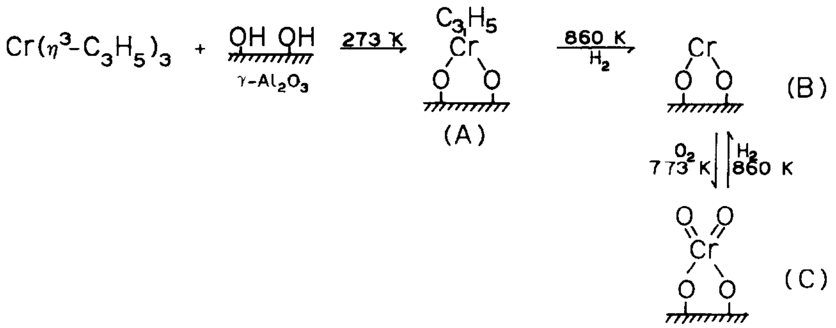
The γ-Al_2O_3-attached Cr(II) dimer and Cr(II) monolayer catalysts which were active for the hydrogenation of propene at low temperatures, were prepared by the reaction between $Cr(\eta^3$-$C_3H_5)_3$ or $Cr_2(\eta^3$-$C_3H_5)_4$ and surface OH groups of γ-Al_2O_3, followed by chemical treatments with H_2. The characterization of the catalyst surfaces was performed by means of IR spectroscopy, temperature-programmed decomposition, UV/VIS diffuse reflectance spectroscopy, ESR, volumetry and chemical analysis.

INTRODUCTION

It has been demonstrated that η^3-allyl complexes of transition metals readily react with surface hydroxyl groups of inorganic oxides such as SiO_2, Al_2O_3, TiO_2, zeolite, etc. (*1–4*) and the obtained surface metal complexes can be converted to their lower or zero-valent levels by reduction with hydrogen at 273–870 K (*3, 4*). Chromium ions supported on Al_2O_3 by a traditional impregnation method are in general hardly reduced to the bivalent level with H_2 or CO. It has been found that the use of $Cr(\eta^3$-$C_3H_5)_3$ provides a way of preparation of the highly active, Al_2O_3-bound Cr(II) monomer catalyst (*5, 6*). In the present paper we report the preparations and characterization of new γ-Al_2O_3-attached Cr(II) dimer and Cr(II) monolayer catalysts. These samples were synthesized by taking advantage of the reaction (*7*) between $Cr_2(\eta^3$-$C_3H_5)_4$ and the surface OH groups of γ-Al_2O_3 followed by chemical treatments with H_2.

EXPERIMENTAL

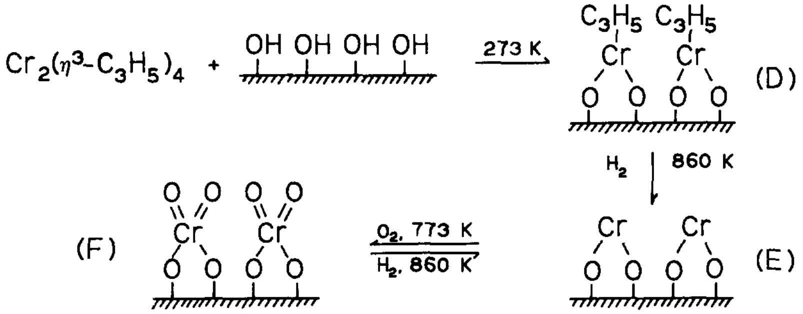
The γ-Al_2O_3-attached Cr(II)-monomer catalyst (B) was prepared according to the following steps as previously reported (*5, 6*):



SCHEME 1

0021-9517/86 $3.00

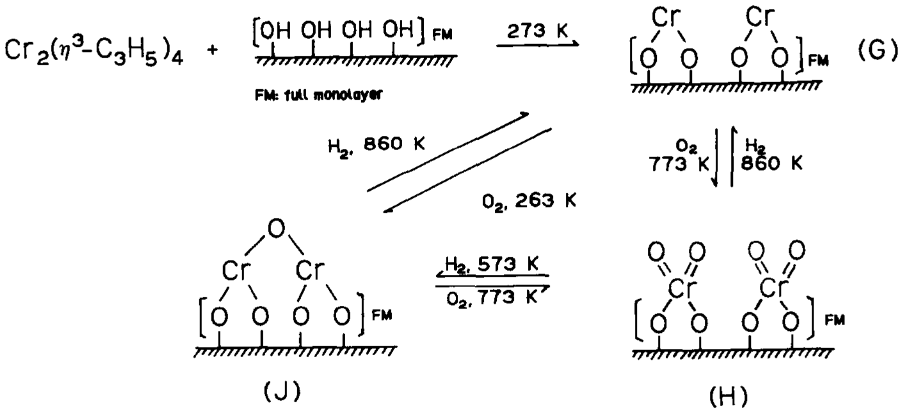
The Cr(II)-dimer catalyst (E) was prepared by the reaction between $Cr_2(\eta^3\text{-}C_3H_5)_4$ (*8*) and the surface OH groups of γ-Al_2O_3 followed by the chemical treatments as described in the previous report (*7*);



SCHEME 2

The concentration of surface OH groups of γ-Al_2O_3 (specific surface area: 190 m^2g^{-1}) used for the preparation of the dimer catalyst was controlled to 2.6 OH nm^{-2} by heating at 773 K for 1.5 h under O_2 pressure of 13.3 kPa and evacuating for 1 h *in situ* before contacting a pentane solution of $Cr_2(\eta^3\text{-}C_3H_5)_4$. The attaching reaction of the Cr complex onto the Al_2O_3 at 273 K was rapid and completed within 20 min.

γ-Al_2O_3 employed for the preparation of a new Cr(II) monolayer catalyst was obtained by calcination of boehmite at 823 K and its surface area was 72 m^2g^{-1}. The γ-Al_2O_3 thus obtained was exposed to water vapor of 2.0 kPa for 5 h at room temperature followed by evacuation at 573 K for 1.5 h; these treatments provided a nearly full monolayer (10 OH nm^{-2}) of OH groups at the γ-Al_2O_3 surface. The OH-covered Al_2O_3 was contacted to a pentane solution of an excess of $Cr_2(\eta^3\text{-}C_3H_5)_4$ at 273 K with stirring. The stirring was continued for 2 h until the surface was saturated with Cr complexes. After decantation of the pentane solution of residual $Cr_2(\eta^3\text{-}C_3H_5)_4$, the surface complex formed by the attaching reaction was washed 3 times with purified pentane under vacuum in order to remove free Cr_2 complexes. The preparation scheme of the new Cr(II) monolayer catalyst is as follows



SCHEME 3

After attaching chromium onto alumina, the pentane used as a solvent for the $Cr_2(\eta^3\text{-}C_3H_5)_4$ complex was evacuated at room temperature for 1 h under the base pressure of 1.33×10^{-3} Pa. Every 0.05–0.3 g of the obtained samples (A), (D), and (G) were divided into U-shaped Pyrex-glass tubes with two break-seals and further treated at 343 K for 1 h under vacuum before use as catalyst. The amount of chromium attached on the support was determined from the initial (before attachment) and the final (after attachment) concentration of $Cr_2(\eta^3\text{-}C_3H_5)_4$ in pentane by a known $FeSO_4$–$KMnO_4$ titration method. The Cr loadings in these catalysts were in the range 0.21–0.91 wt%.

The UV/VIS diffuse reflectance spectra (DRS) were measured after various treatments of samples in a thin quartz cell combined to a closed circulating system on a JASCO UVIDEC-500 spectrometer. The IR spectra of the surface allyl-type complex were recorded in a quartz cell with two NaCl windows by a self-supported disk method on a JASCO IR-810 spectrometer. The temperature-programmed decomposition (TDPE) chromatograms of the surface complexes were taken in a closed-circulating-type TPDE apparatus (a flow of hydrogen of 9.3 kPa) connected to gas chromatography using a column of 5A molecular sieve (1.5 m) and a column of VZ-10 (2 m). The O_2 or H_2 uptakes in O_2 oxidation or H_2 reduction of the Cr samples were volumetrically measured.

RESULTS

Cr(II)-Dimer Catalyst

The new γ-Al_2O_3-attached Cr(II)-dimer catalyst (E) was obtained by removal of the allyl ligands of species (D) with H_2. The IR spectra of species (D) after evacuation at various temperatures are shown in Fig. 1 where the C–C stretching-frequency peaks for all the samples were observed at 1563 cm^{-1} except for a low-temperature-treated sample. The sample evacuated at 313 K showed a more broad peak. Besides the main peak at 1563 cm^{-1} a small peak was observed at 1461 cm^{-1} which may be assignable to a CH_2 deformation mode. The peaks disappeared by reduction with H_2 at 823 K for 1 h.

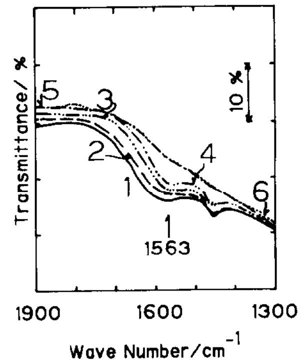


FIG. 1. IR spectra of Al_2O_3-attached $Cr_2(\eta^3\text{-}C_3H_5)_4$ after various treatments. (1) Evacuation at 313 K for 1 h, (2) evacuation at 355 K for 1 h, (3) evacuation at 423 K for 30 min, (4) evacuation at 523 K for 30 min, (5) reduction with H_2 (7.3 kPa) at 823 K for 1 h, (6) background (Al_2O_3).

The TPDE chromatogram of the allyl species (D) under circulation of a reduced pressure of H_2 (9.3 kPa) was taken in order to know the number of allyl ligands coordinated to a Cr atom, the degree of homogeneity of the Cr species (D) and the thermal stability in comparison with a $Cr_2(\eta^3\text{-}C_3H_5)_4$ complex. The chromatogram in Fig. 2 showed a main peak for propene evolution at 599 K together with a propane peak at a similar temperature. Besides these major products small amount of ethene and ethane were evolved around 720 K and methane was also observed above 593 K in Fig. 2. Small amounts of carbon remained at the catalyst surface after the ligand decomposition (C/Cr < 0.11 in an atomic ratio); these were analyzed as CO_2 by oxidizing with O_2 at 773 K. The number of allyl ligands on a Cr ion in the surface complex (D) was calculated from the equation, $\left(\sum_{i=1}^{3} iC_i + CO_2\right)/3$, as previously described (5). The value is given in Table 1, which indicates that the structure (D) had one allyl ligand per Cr

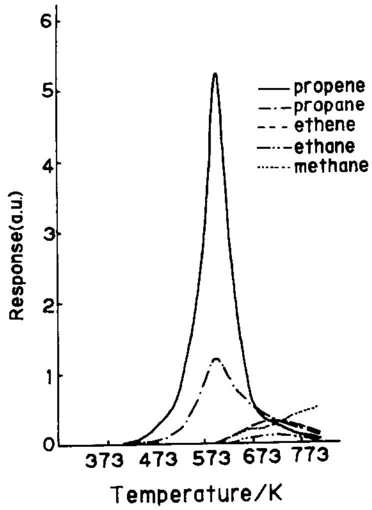


FIG. 2. Temperature-programmed decomposition (TPDE) chromatogram of the Cr-allyl dimers (D) attached to γ-Al_2O_3; heating rate: 4 K min^{-1}.

atom. The composition of the surface complexes was essentially the same for the two kinds of γ-Al_2O_3 used in the present study.

The surface species (D) was transformed to Cr(II)-dimers (E) with reduction with H_2 at 860 K. The (E) was further converted to Cr(VI)-dimers (F) with stoichiometric oxidation with O_2 as shown in Scheme 2 and Table 1. These steps were followed by means of DRS. Figure 3 shows the DRS spectra of the γ-Al_2O_3-attached Cr-dimer catalyst and the impregnation Cr catalyst under various conditions. The 380-nm peak of the traditional impregnation Cr(VI) catalyst obtained by calcination of impregnated chromic acid at 823 k in Fig. 3b is assigned to the charge transfer band of $Cr^{6+} = O^{2-}$ in a monochromate structure. Besides the Cr^{6+} peak a shoulder at ca. 600 nm also implies the presence of Cr^{3+} species. When the impregnation Cr(VI) catalyst was reduced to $Cr^{2.15+}$ level on average with H_2 at 860 K for 2 h in a closed circulating system with a U-shaped liquid-N_2 trap placed soon after the catalyst, a complicated spectrum with a peak position at 439, 585, 650, 713, and 810 nm in Fig. 3b was observed, suggesting a mixture of Cr species in different oxidation states and environments. The spectrum of the surface species with an allyl ligand (D) showed two peaks at 470 and 610 nm in Fig. 3a. The broad ESR spectrum with $g = 2.03$ and $\Delta H = 1300$ G was observed. The Cr(II)-dimers (E) obtained from (D) exhibited main DRS peaks at 615

TABLE 1

Stoichiometric Behaviors in the Reduction and Oxidation of the Attached Cr Catalysts

Catalysts	Monomer[a]	Dimer[b]	Monolayer
Chemical analysis of Cr (wt% as Cr/Al_2O_3)	0.91	0.49	0.24
Number of C_3-ligand/Cr in the surface complex	1.04	1.1	<0.15
O_2 uptake/Cr in the step,			
$Cr^{2+} \rightarrow Cr^{6+}$	0.99	0.99	1.04
$Cr^{2+} \rightarrow Cr^{3+}$	—	—	0.27
H_2 uptake/Cr in the step,			
$Cr^{6+} \rightarrow Cr^{2+}$	2.04	1.98	2.02
$Cr^{6+} \rightarrow Cr^{3+}$	—	—	1.57

[a] Similar values in the range of Cr-loadings 0.21–0.91 wt%.

[b] Similar values in the range of Cr-loadings 0.36–0.78 wt%.

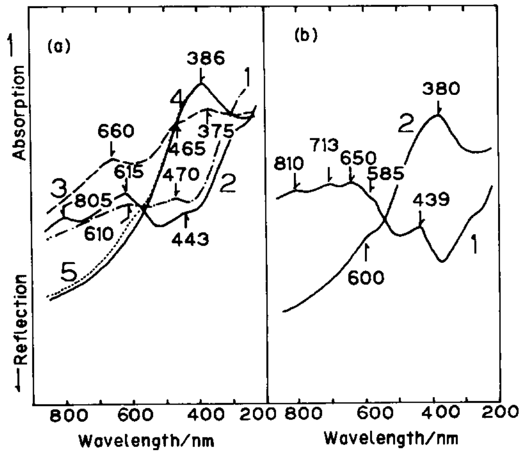
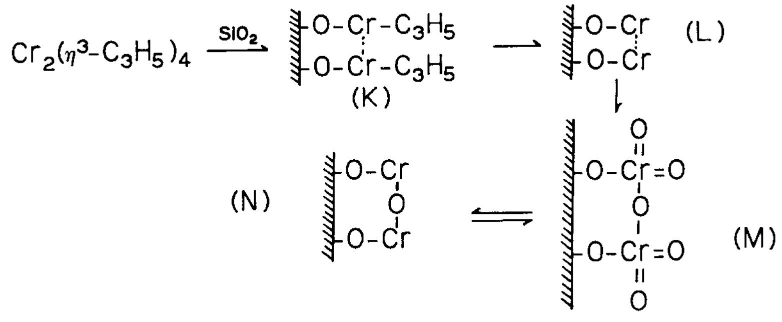


FIG. 3. DRS spectra of the attached (a) and impregnation (b) Cr catalysts. (a): (1) Cr(III)-allyl dimer (D), (2) Cr(II)-dimer (E), (3) Cr(IV)-dimer (O), (4) Cr(VI)-dimer (F), (5) Cr(VI)-dimer catalyst, rearranged by repeated reduction–oxidation cycles. (b) (1) Reduced catalyst ($Cr^{2.15+}$), (2) oxidized catalyst.

and 805 nm, and also a small peak at 443 nm. When the Cr(II) species was carefully and slowly exposed to oxygen of 6.6 kPa at room temperature, new peaks at 375, 465, and 660 nm were developed. The Cr(II) species (E) was oxidized with O_2 at 773 K to give the Cr(VI) spectrum (λ_{max}: 386 nm) in Fig. 3a.

The Cr(II)-dimers attached on SiO_2 instead of γ-Al_2O_3 showed a much lower activity than the Al_2O_3-attached catalyst (E) in the hydrogenation of propene (*7*). The DRS spectra of the SiO_2-attached species in Fig. 4 were taken for comparison with those in Fig. 3a.



SCHEME 4

The Cr(II)-allyl dimers (K) on SiO_2 depicted a characteristic peak at 553 nm which is assigned to $\delta \rightarrow \delta^*$ transition for the Cr(II) dimer structure with a direct Cr(II)–Cr(II) bond. On removing the allyl ligand with H_2 at 860 K, the structureless spectrum of Cr ions (L) in a univalent level was observed. This species was oxidized to the dichromate (VI) species (M) with O_2 at 773 K which showed a characteristic peak at 485 nm. The spectrum of Cr(II) dimers (N) obtained by reduction of (M) is shown in Fig. 4 where a main peak at 800 nm together with 460- and 620-nm peaks was observed.

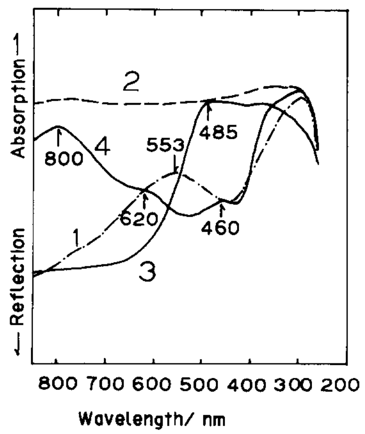


FIG. 4. DRS spectra of the SiO_2-attached Cr-dimer catalysts. (1) Cr(II)-allyl dimers (K), (2) Cr(I)-dimers (L), (3) Cr(VI)-dimers (M), (4) Cr(II)-dimers (N).

Cr(II)-Monolayer Catalyst

The attachment of $Cr_2(\eta^3$-$C_3H_5)_4$ onto the OH-covered γ-Al_2O_3 surface provided the Al_2O_3-attached Cr-monolayer catalyst (G). Figure 5 shows the TPDE chromatogram for the γ-Al_2O_3-attached Cr(II) assembly in monolayer (G). The amount of products desorbed was much less than that for the species (D) in Fig. 2. A main product was propene similarly to the case of the dimer, but the peak position (543 K) was lower by 56 K as compared with the peak for (D). Another different feature of Fig. 5 from Fig. 2 is the evolution of 1-butene. The carbon amounts deposited at the surface after the TPDE analysis were negligible ($C/Cr < 0.03$). Consequently, the total amount of the C_3H_5 ligands remained in the species (G) after attaching $Cr_2(\eta^3$-$C_3H_5)_4$ onto the full-monolayer OH surface was found to be

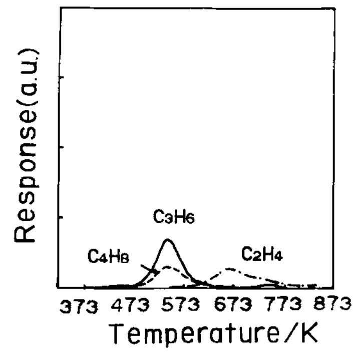


FIG. 5. TPDE chromatogram of the γ-Al_2O_3-attached Cr-monolayer species (G); heating rate: 4 K min^{-1}. The scale in the ordinate is expanded as compared with that in Fig. 2.

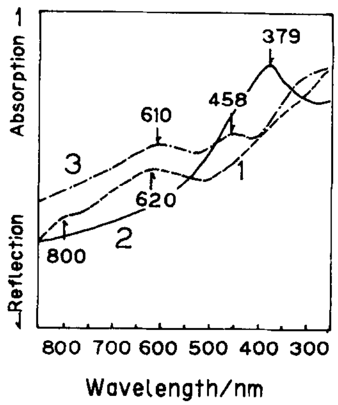


FIG. 6. DRS spectra of the Cr-monolayer catalysts. (1) Cr(II) (G), (2) Cr(VI) (H), (3) Cr(III) (J).

no more than 15% of the amount of Cr ions contained.

The DRS spectra of the Cr(II) monolayer assembly (G) attached on γ-Al_2O_3 are shown in Fig. 6. The DRS spectrum of the (G) showed a main peak at 620 nm with a small peak at 800 nm in contrast to the spectrum (Fig. 3) of species (D) made by the reaction between $Cr_2(\eta^3\text{-}C_3H_5)_4$ with a γ-Al_2O_3 surface with OH groups of 2.6 OH nm^{-2}. The species (G) was further treated with H_2 at 860 K for 30 min and then oxidized to the Cr(VI) monolayer catalyst (H) with O_2 at 773 K, uptaking the quantitative amount of O_2 as given in Table 1. The Cr(VI) catalyst (H) had only a peak at 379 nm similarly to the Cr(VI) dimers (F). The Cr(VI) assembly in monolayer was found to be transformed to Cr(III) surface (J) by mild reduction with H_2 at 573 K as shown in Scheme 3. The (J) was also obtained by stoichiometric oxidation of the Cr(II) monolayer with O_2 at 263 K. The DRS peaks of the Cr(III) monolayer (J) were observed at 458 and 610 nm as shown in Fig. 6.

Each step of the transformation in Scheme 3 was also volumetrically analyzed by the measurements of the amount of H_2 or O_2 consumed in the reduction or oxidation as shown in Fig. 7. The Cr(II) assembly (G) was quantitatively oxidized to the tervalent level (J) with O_2 at 263 K and then with oxidation at 773 K to the Cr(VI) ions (H), uptaking the stoichiometric amounts of O_2. Reversely, the Cr(VI) species (H) was transformed to the Cr(III) species (J) by reduction with H_2 at 573 K, and at 853 K to the Cr(II) assembly (G) again as shown in Fig. 7.

DISCUSSION

Figure 2 shows a single peak for propene at 599 K together with a peak for propane at a similar temperature; other products like ethene, ethane, and methane are relatively negligible. The relative ratio of propane to propene reflects the relative probability in the reaction steps, $C_3H_5(ad) + \frac{1}{2}H_2 \rightarrow C_3H_6$ and $C_3H_5(ad) + \frac{3}{2}H_2 \rightarrow C_3H_8$. The peak temperatures were almost constant in the range of Cr-loadings 0.21–0.91 wt%. The TPDE

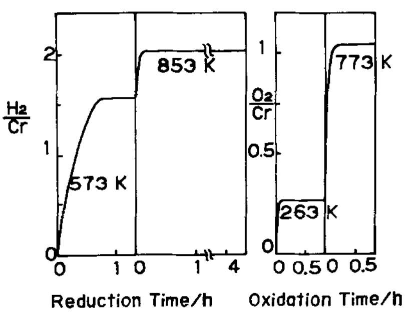


FIG. 7. Stoichiometric behaviors of the attached Cr species in the reduction of Cr(VI) monolayer (H) and the oxidation of Cr(II) monolayer (G).

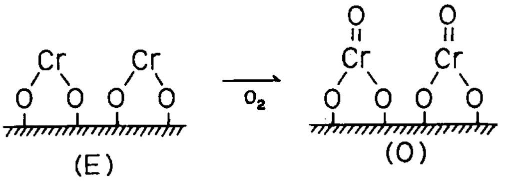
analyses indicate that the majority of the Cr-dimer species were uniformly distributed on the γ-Al_2O_3 surface. The C–C stretching band of allyl ligands in the species (D) was observed at 1563 cm^{-1} as shown in Fig. 1 where a small peak at 1461 cm^{-1}, assignable to a CH_2 deformation mode, was also observed. The C–C stretching frequency is different from 1520 cm^{-1} (π-allyl type) for $Cr(\eta^3$-$C_3H_5)_4$ and also from near 1620 cm^{-1} for η^1-C_3H_5 (σ-allyl type). We propose that the allyl ligands of (D) are of η^2-type (or dynamic σ-allyl type). The decrease in the peak intensity by heating to 523 K in Fig. 1 is compatible with the TPDE curve in Fig. 2. As seen in Fig. 2, the surface-attached η^2-allyl ligand of (D) was much more themostable than the original $Cr_2(\eta^3$-$C_3H_5)_4$ complex. The amount of the C_3H_5 groups coordinated on a Cr atom is given in Table 1, which indicates that the structure (D) had one allyl ligand per Cr atom; that is, two allyl ligands of $Cr_2(\eta^3$-$C_3H_5)_4$ were lost by reaction with two OH groups with a concomitant oxidation of Cr from 2+ to 3+. The oxidation state of Cr atom in (D) was also confirmed by the DRS spectrum in Fig. 3. The peaks at 470 and 610 nm are assigned to the *d–d* transitions for d^3 ions. The dependence of the ESR peak intensity ($g = 2.03$, $\Delta H = 1300$ G) of (D) upon temperature suggested a weak, direct exchange interaction between two adjacent Cr^{3+} ions. The TPDE peaks for (D) were observed at higher temperatures by about 90 K than those of the peaks for the monomer (A), reflecting a difference of (A) and (D) in the environments of Cr(III) species. These results demonstrate that two Cr atoms of a $Cr_2(\eta^3$-$C_3H_5)_4$ dimer were chemically and adjacently attached to form the structure (D) in Scheme 2.

In contrast to the formation of the Cr(III)-allyl dimers (D), the attaching reaction of an excess of $Cr_2(\eta^3$-$C_3H_5)_4$ with the γ-Al_2O_3 surface covered with full-monolayer OH groups led to the formation of the Cr species (G) which showed very small TPDE peaks as shown in Fig. 5. The amount of allyl groups remained at the surface after the attaching reaction was calculated to be as few as 0.15 C_3H_5 per Cr atom; 92.5% of the allyl ligands of $Cr_2(\eta^3$-$C_3H_5)_4$ were lost by reaction with surface OH groups. The saturation mass of attachment of the Cr species was 0.24 wt% as Cr/Al_2O_3 when the γ-Al_2O_3 (surface area = 72 m^2g^{-1}; pore diameter at maximum in the distribution = 2 nm) was employed. The saturation mass implies that a $Cr_2(\eta^3$-$C_3H_5)_4$ molecule solvated with pentane molecules could not enter the pores of support which diameter are smaller than about 3.5 nm. The Cr dimers initially attached at the pore entrance may interfere the subsequent entering of the Cr dimer complexes into the pore. The monolayer-covered Cr species (G) thus obtained consumed two oxygen atoms per Cr atom to be oxidized to the monochromate (VI) structure (H) with O_2 at 773 K as given in Table 1; the (H) depicted a peak at 379 nm assigned to a charge transfer band ($^1A_1 \rightarrow {^1T_2}$ (*9*) of a monochromate structure in Fig. 6. The stoichiometry suggests that the Cr ions (G) in monolayer with almost no C_3H_5 ligands were genuinely in a bivalent level. The bivalency of the naked Cr ions in (G) is also shown in Fig. 6 where the DRS peaks at 620 and 800 nm were observed and no distinct peaks for Cr(III) ions appeared at 400–500 nm; the spectrum is entirely different from those of Cr(III)-allyl species (D) (Fig. 3) and Cr(III)-oxide species (J) (Fig. 6).

The Cr(III)-C_3H_5 dimers (D) almost uniformly distributed on γ-Al_2O_3 were reduced to the Cr(II) level (E) by treatments with H_2 in Scheme 2. The (E) showed two peaks at 615 and 805 nm in Fig. 3 similarly to the (G) in Fig. 6. Again, the O_2 titration at 773 K confirmed the bivalency of (E) as given in Table 1. The remained question is which symmetry the Cr(II) ions are situated in. The peak near 800 nm may be referred to tetrahedral Cr(II) ions (*10, 11*). The Cr(II) ions (N) attached on SiO_2 showed a peak at 800 nm in Fig. 4 where minor peaks at 460 and 620 nm are due to Cr(III) ions, but its amount seems to be a few percents of total Cr taking into account the larger molar extinction coefficient of *d–d* transition of d^3 ions as compared with that of d^4 ions. Thus, the Cr(II) ion on SiO_2 is an example situated in T_d symmetry. On the other hand, the peaks at 615 nm in Fig. 3 or 620 nm in Fig. 6 might be assigned to the transition $^5E_{2g} \rightarrow {}^5T_{2g}$ for an octahedral Cr(II) species (*12*). However, the monomer species (B) which had three vacant coordination sites on a Cr(II) ion as previously reported (*5*) showed the DRS peaks at 610 and 800 nm. The coordinatively unsaturated site of the Cr(II) ion of (E) was also estimated to be about 2 from the adsorption measurements of N_2 or O_2 at 176 K. These results exclude octahedral symmetry for Cr(II) ions attached on γ-Al_2O_3 surface. Although the number of the adsorption sites of (E) was smaller than that of (B), the environment of the Cr(II) ions of the dimer (E) was spectroscopically similar to that of the Cr(II) monomers (B). Kellerman and Klier observed the peaks at 590 and 830 nm for Cr(II) ions in A zeolite located in D_{3h} symmetry (*13*). These results indicate that the Cr(II) ions in (B), (E), and (G) are situated in near C_{3V} symmetry, where the peaks at 610–620 and 800–805 nm are assigned to $^5E \rightarrow {}^5A$, and $^5E \rightarrow {}^5E$, respectively, for a trigonal conformation of d^4 ion.

The Cr(II)-allyl dimer (K) attached on SiO_2 exhibited a characteristic absorption peak at 553 nm (Fig. 4) which is assignable to $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition for dinuclear Cr(II)–Cr(II) structure as previously reported (*14*). The bond distance between two adjacent bivalent chromiums of the dimer (K) was estimated to be 0.222 nm, assuming a linear relation between the distance of the metal–metal bond and the energy (18.1×10^3 cm^{-1}) of the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition (*15*). The Cr–Cr separation is much longer than 0.1975 nm for the original $Cr_2(\eta^3\text{-}C_3H_5)_4$ complex. In contrast, the DRS spectra of (E) and (G) provided no information on direct bonding between the two adjacent Cr(II) ions in the dimer structure (E) and the monolayer assembly (G). Good EXAFS spectra of the samples were not obtained owing to their low Cr-loadings below 1 wt%.

When the Cr(II) dimers (E) were carefully oxidized with O_2 at room temperature, new peaks at 375, 465, and 660 nm appeared as shown in Fig. 3. These absorption peaks, similar to those of Cr(IV) ions in A-zeolite (*13*), are ascribed to Cr(IV) in distorted tetrahedral symmetry. It is likely that the irreversible oxidation of trigonal Cr(II) to tetrahedral Cr(IV) occurs in the following manner:



SCHEME 5

It is to be noted that the Cr(II) monolayer (G) was quantitatively oxidized to Cr(III) level (J) with O_2 at 263 K as shown in Fig. 6 and Table 1, reflecting a difference in the arrangements of Cr(II) ions (dimers or assembly). The (J) was converted to the monochromate (VI) structure (H) by oxidation with O_2 at 773 K as shown in Fig. 7, Fig. 6, and Scheme 3. Reversely, the Cr(VI) monolayer (H) was mildly reduced to the Cr(III) monolayer (J) with *d–d* peaks at 458 nm ($^4A_{2g} \rightarrow {}^4T_{2g}$) and 610 nm ($^4A_{2g} \rightarrow {}^4T_{1g}$) again, uptaking a stoichiometric amount of H_2 at 573 K as shown in Figs. 6 and 7. The (J) was further reduced to (G) with H_2 at 860 K. The stoichiometric behaviors of attached Cr species in reduction and oxidation steps are given in Table 1. In general, the surfaces of the attached Cr(II) catalysts obeyed gradual rearrangements during repeated oxidation–reduction cycles at 860 K. The rearranged Cr(II) surface contained small amount of Cr(III) ions.

The traditional Al_2O_3-supported Cr catalysts in both oxidized and reduced states showed complicated Cr spectra (Fig. 3) as compared with the attached Cr catalysts. A few different species seem to be always present in the impregnation catalysts and the extent of reduction is not clean (*16*).

It was found that the Al_2O_3-attached Cr(II) monomer (B), Cr(II) dimer (E), and Cr(II) monolayer (G) catalysts were highly active for the hydrogenation of propene at 195–261 K. The details of catalytic reactions on the Cr(II) catalysts will be reported in the following paper (*17*).

REFERENCES

1. Ballard, D. G. H., "Advances in Catalysis," Vol. 23, p. 263. Academic Press, New York, 1973.

2. Candlin, J. P., and Thomas, H., *Adv. Chem. Ser.* **132,** 212 (1974).

3. Yermakov, Yu. I., Kuznetsov, B. N., and Zakharov, V. A., "Catalysis by Supported Complexes." Elsevier, Amsterdam, 1981.

4. Iwasawa, Y., "Tailored Metal Catalysts." Reidel, Holland, 1986.

5. Iwasawa, Y., *J. Mol. Catal.* **17,** 93 (1982).

6. Iwasawa, Y., and Ogasawara, S., *Chem. Lett.* **1980,** 127.

7. Iwasawa, Y., Sasaki, Y., and Ogasawara, S., *J. Chem. Soc., Chem. Commun.*, 140 (1981).

8. Wilke, G., Bogdanovic, B., Hardt, P., Heimbach, P., Keim, W., Kröner, M., Oberkirch, W., Tanaka, K., Steinrücke, E., Water, D., and Zimmermann, H., *Angew. Chem. Int. Ed. Engl.* **5,** 151 (1966); Becconsall, J. K., and O'Brien, S., *J. Chem. Soc. A,* 423 (1967).

9. Carrington, A., and Symons, M. C. R., *Chem. Rev.* **63,** 443 (1963); Viste, A. and Gray, H. B., *Inorg. Chem.* **3,** 1113 (1964).

10. Krauss, H. L., *in* "Proceedings, 5th International Congress on Catalysis, Amsterdam, 1964," Vol. 8, p. 207. Wiley, New York, 1973; Krauss, H. L., and Westphal, U., *Z. Naturforsch. B* **33,** 1278 (1978).

11. Kazansky, V. B., *Kinet. Katal.* **11,** 455 (1970).

12. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C., and Borello, E., *J. Phys. Chem.* **79,** 966 (1975).

13. Kellerman, R., and Klier, K., "Molecular Sieves II," p. 120. Amer. Chem. Soc., Washington, D.C., 1977.

14. Iwasawa, Y., Sasaki, Y., and Ogasawara, S., *J. Mol. Catal.* **16,** 27 (1982).

15. Cotton, F. A., *Acc. Chem. Res.* **11,** 225 (1978); Sattelberger, A. P., and Fackler, J. D., *J. Amer. Chem. Soc.* **99,** 1258 (1977); Cotton, F. A., Koch, S., Mertis, K., Millar, M., and Wilkinson, G., *J. Amer. Chem. Soc.* **99,** 4989 (1977); Bömer, W. H., Madeja, K., Kurras, E., and Rosenthal, U., *Z. Chem.* **18,** 453 (1978).

16. Clark, A., *Catal. Rev.* **3,** 145 (1969).

17. Iwasawa, Y., Chiba, T., and Ito, N., to be published.