J. Phys. Chem. A **1998,** *102,* 7913−7918

Behavior of Chromium Oxide on MgO or MgF_2

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Received: April 21, 1998; In Final Form: August 10, 1998

The molecular structure and oxidation state of the chromium oxide on MgO or MgF_2 as a function of Cr loading were determined by XRD, Raman spectroscopy, and XPS. The effects of preparation method and the acidity of support were investigated. The Raman study on a series of chromium oxide supported on MgO prepared by an impregnation method showed that the chromium oxide was present as polychromate independent of Cr loading due to high acidity of the preparation solution. In samples prepared by a precipitation method, the chromium oxide was present as monochromate at 5% Cr loading, as dichromate at 10% Cr loading, and as mono- and polychromate at 20% Cr loading due to a larger surface area of the support prepared by this method. The chromium in CrO_3/MgF_2 was present as polychromate and monochromate for impregnated and precipitated samples, respectively. The oxidation state of Cr(VI) on MgO is maintained independent of Cr loadings. When the 10 wt % Cr/MgO was calcined at 800 °C, $MgCr_2O_4$ and Cr_2O_3 were formed. Preferred formation of $MgCr_2O_4$ was observed for the precipitated sample due to its larger surface area compared to that of the impregnated sample.

Introduction

The behavior of chromium oxides supported on metal oxides has been extensively studied, due to their activity in several catalytic processes of polymerization, isomerization, dehydrogenation, aromatization, and oxidation. The identification of the molecular structure of surface Cr species have been accomplished on Al_2O_3, SiO_2, ZrO_2, and TiO_2. These materials have been extensively characterized by different spectroscopic techniques: Raman spectroscopy,[1−11] diffuse reflectance spetroscopy (DRS),[12−20] IR spectroscopy,[21,22] electron paramagnetic resonance (EPR),[23−26] and X-ray photoelectron spectroscopy (XPS).[27−30] There is now a general consensus that different oxidation states of Cr can be present depending on the pretreatment conditions and that the dispersion of Cr is a function of support type/composition, pretreatment condition, and chromium oxide loading. At low values of Cr loading, the oxidation state is predominantly Cr(VI) after calcination in air at 773 K, whereas the Cr(III) phase appears in catalysts of higher chromium content. The behavior of chromium oxide supported on MgO or MgF_2 has not been discussed in the literature. Although the MgO support has a basic character, CrOx/MgO catalysts have been used in catalytic reactions such as the synthesis of 2,6-dimethylphenol from methanol and cyclohexanol.[31] MgF_2 has also drawn attention as a support due to the fact that, when it was used as a support for transition metal oxides, it generates new acid−base and redox active sites useful for the reactions of 2-propanol decomposition, butene double-bond isomerization, cumene cracking, dehydrogenation of cyclohexane, and decomposition of methyl alcohol.[32]

The aim of this work is to characterize the chromium oxide supported on MgO or MgF_2. The influences of the Cr loading and calcination temperature were studied on the structure of chromium(VI) oxide supported on MgO. A pore-filling impregnation method was compared with a precipitation method in this respect. In contrast to MgO, MgF_2 has a strong acidic property. Thus, the chromium structure may be different in two supports. On the basis of XRD, Raman, and XPS, we attempted to determine the chromium structure and the oxidation state of supported chromium oxide.

Experimental Section

Sample Preparation. Two series of CrO_3/MgO samples were prepared: one by impregnation and the other by precipitation−deposition. Impregnated samples were obtained by pore-filling impregnation of a MgO powder (Alfa, surface area 10 m^2/g) with an aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ (Aldrich). The MgO support was checked by XPS for the potential presence of basic impurities such as Ca, Na, K, etc., and none was found. Following impregnation, the samples were dried in air at 110 °C for 12 h and calcined at 400, 600, or 800 °C for 4 h. The Cr content of 1, 5, 10, or 20% was employed.

Precipitation was accomplished from an aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ of a known concentration onto suspended particles of MgO (10 m^2/g). The resulting precipitated slurry was aged for 10 h in the same stirring vessel to complete the precipitation. It was then filtered and washed several times with distilled water and dried in an oven at 110 °C for 12 h and then calcined at 400, 600, or 800 °C for 4 h. The loading of Cr was 5, 10, or 20 wt %.

CrO_3/MgF_2 samples were also prepared by the pore-filling impregnation and precipitation methods. For the precipitation method, MgF_2 and an aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ were introduced into a stirred vessel, and an aqueous solution of ammonia was slowly added to the vessel. The final pH was set equal to 8.0, and the precipitated slurry was kept stirred so as to complete the precipitation. It was filtered and washed several times with distilled water and dried in an oven at 110 °C for 12 h and then calcined at 400 °C for 4 h. The MgF_2

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S1089-5639(98)01927-6 CCC: \$15.00

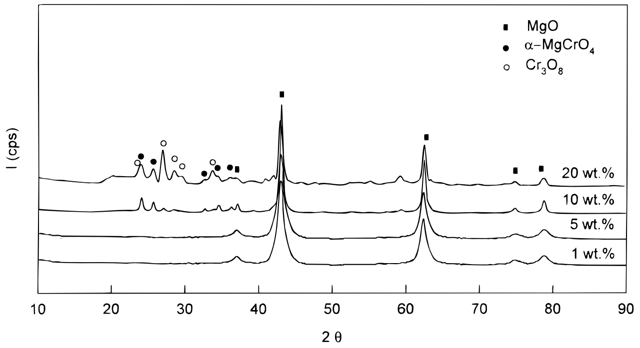


Figure 1. XRD patterns of CrO_3/MgO prepared by the impregnation method, calcined at 400 °C, as a function Cr loading.

support (182.9 m^2/g) was prepared from a reaction between MgO and an HF solution. All loadings are expressed in weight percent Cr.

Techniques. X-ray diffraction measurements were performed using a Rigaku DMAX-B diffractometer with Cu Kα radiation. The scan rate was 4° min^{-1} and the range of scan (2θ) was 10−90°. The specific surface area was determined by the N_2 BET method on a constant volume adsorption apparatus.

XPS measurements were performed on a Perkin-Elmer PHI 5400 ESCA spectrometer with monochromatic Mg Kα radiation and a pass energy of 80 eV. Binding energies were corrected for surface charge by referencing them to the energy of C 1s peak at 284.6 eV.

Raman spectra were recorded from powdered sample pressed into self-supporting wafers. The spectra were obtained in the 180° configuration on a 532-RENS-A01 model, using the 514.5 nm radiation of argon ion gas as the excitation source. The laser power at the sample wafers was 4 mW, and the spectral resolution was 3−4 cm^{-1}. The scattered radiation was detected by Wright instruments with an intensified photodiode array cooled thermoelectrically to −30 °C. The Raman spectra were recorded using an OMA III dedicated computer and software. All Raman spectra were obtained at room temperature and under ambient conditions.

Results

CrO_3/MgO Prepared by Impregnation. The results of XRD analyses for CrO_3/MgO (calcination at 400 °C) with different Cr loadings are shown in Figure 1. The samples loaded with 1 and 5 wt % Cr showed only peaks of MgO, indicating a high dispersion of chromia. Above 10 wt % of Cr loading, several new peaks appeared that could be assigned to Cr_3O_8 and α-$MgCrO_4$ structures. As the Cr loading increased from 10 to 20 wt %, the intensity of Cr_3O_8 peaks increased. The formation of α-$MgCrO_4$ structure indicates that a solid-state reaction has occurred between Cr and the support at 400 °C.

Figure 2 shows the effect of the calcination temperature on the structure of chromium supported on MgO. The sample containing 10 wt % Cr was calcined at 400, 600, or 800 °C for 4 h. There was no difference in the XRD pattern between samples calcined at 400 and 600 °C. However, the XRD pattern of the sample heated at 800 °C showed new peaks, indicating the formation of $MgCr_2O_4$ structure. $MgCr_2O_4$ is known to be prepared by firing MgO and Cr_2O_3 at 1200 °C for 50 h.[29] Thus, the chromium oxide structure on the MgO support remains the same at calcination temperatures of 400 and 600 °C. When the sample is calcined at 800 °C, however, the chromium oxide is transformed to $MgCr_2O_4$.

The Raman spectra of a series of chromium oxide on MgO are presented in Figure 3 as a function of the chromium oxide loading. The assignment of these spectra was based on literature data in aqueous solutions presented in Table 1. In general, an aqueous solution of chromium(VI) oxide compounds possesses strong Raman bands in the 800−1000 cm^{-1} region due to Cr−O stretching modes and bands of moderate intensity in the 300−400 cm^{-1} region due to the Cr−O bending modes. The band positions of our samples exhibit the presence of Cr(VI) oxides species, and the oxidation state is confirmed by XPS. The observed spectra are quite similar for all loadings with Raman bands at 965, 930, 906, 848, 400, and 365 cm^{-1}. According to the literature, the Raman bands at 962, 904, 846, 378, and 217 cm^{-1} have been observed for aqueous chromium solutions under extreme conditions of strong acidity and high chromium contents.[33] They were then assigned to the trichromate ion, $Cr_3O_{10}^{2-}$ (**I**), and the tetrachromate ion, $Cr_4O_{13}^{2-}$ (**II**). Taking into account of the structure of these ions, the Raman bands are tentatively assigned as follows: 962 cm^{-1}, $\nu_s(Cr''O_2)$; 904 cm^{-1}, $\nu_s(Cr'O_3)$; 846 cm^{-1}, $\nu_s(OCr''O)$; 378 cm^{-1}, $\delta(Cr'O_3)$;

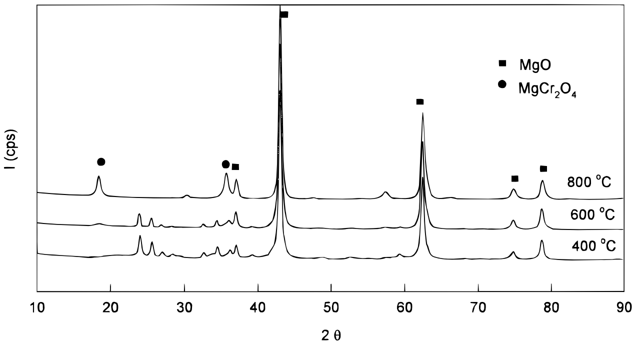


Figure 2. XRD patterns of CrO_3/MgO prepared by the impregnation method, as a function of calcination temperature, at a fixed Cr loading of 10 wt %.

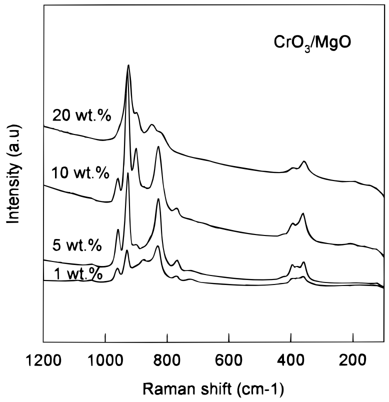


Figure 3. Raman spectra of CrO_3/MgO prepared by the impregnation method, calcined at 400 °C, as a function Cr loading.

TABLE 1: Raman Band Assignments (in cm^{-1}) of Chromium(VI) Oxide Species in Solutions[8,33−36 a]

CrO_4^{2-}(aq)	$Cr_2O_7^{2-}$(aq)	$Cr_3O_{10}^{2-}$(aq)	$Cr_4O_{13}^{2-}$(aq)	assignment
			987	$\nu_{as}(Cr''O_2)$
		962	963	$\nu_s(Cr''O_2)$
884	943			$\nu_{as}(Cr'O_3)$
847	904	904	902	$\nu_s(Cr'O_3)$
	776			$\nu_{as}(Cr'OCr'')$
		846	842	$\nu_s(OCr''O)$
	557		525	$\nu_s(Cr'OCr'')$
368	367	378	365	$\delta(Cr'O_3)$
348			348	$\delta(Cr'O_3)$
	217	217	209	$\delta(Cr'OCr'')$

[a] ν_{as} and ν_s = asymmetric and symmetric stretching modes; δ = bending modes.

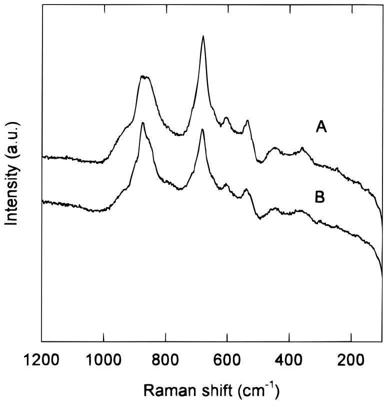


Figure 4. Raman spectra of 10 wt % CrO_3/MgO calcined at 800 °C prepared by different methods: (A) precipitation (B) impregnation.

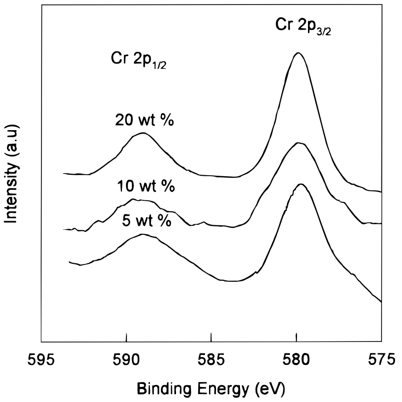
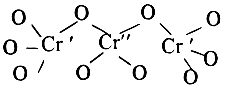
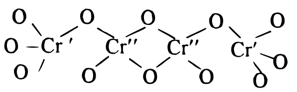


Figure 5. XPS spectra of CrO_3/MgO prepared by the impregnation method, calcined at 400 °C, as a function Cr loading.



(I)



(II)

217 cm^{-1}, δ(Cr′OCr″). In our case of supported Cr species, the bending modes were weak and poorly resolved at 217 cm^{-1}. The Raman peak at 930 cm^{-1} can be assigned to the ν_s(Cr′O_3) mode shifted from 904 cm^{-1}, which is caused by increased interaction between the chromium oxide species and the support. The Raman peak at 930 cm^{-1} is in agreement with that reported by Vuurman et al.[8] for chromium oxides supported on Al_2O_3. The bending mode of (Cr′O_3) is found at 365 cm^{-1}. The intense 800−960 cm^{-1} Raman band is assigned to the stretching mode of Cr−O−Cr groups with an oxygen making a bridge between two chromium cations and suggests that tri- and tetrachromium species are present in these samples. The presence of oligomeric species is supported by the 770 and 400 cm^{-1} bands, which are assigned to ν_{as}(CrOCr) and δ(CrO_2), respectively. The relative intensities of ν_s(Cr″O_2)/ν_s(Cr′O_3) decrease with increasing Cr loading, indicating that the species possessing a terminal CrO_3 units increased due to increasing Cr_3O_8 structure. At very low Cr loading (1%), additional weak Raman bands are observed at 880 cm^{-1}, which are due to chromium oxide monomers [CrO_4]. This Raman band is in agreement with that reported by Hardcastle and Wachs[1] for chromium oxide supported on Al_2O_3, TiO_2, and SiO_2. Thus, there are mono- and polychromates in 1 wt % Cr/MgO.

The influence of calcination temperature upon Raman spectra of 10 wt % Cr/MgO samples was also examined. The Raman spectra of the samples prepared by precipitation and impregnation and calcined at 800 °C are shown in Figure 4. The samples exhibit Raman bands at 880 cm^{-1} due to the symmetric stretch of the surface chromate species (Cr−O) and a new intense peak at 680 cm^{-1} which may originate from a $MgCr_2O_4$ structure. The Raman band at 540 cm^{-1} is assigned to the crystalline Cr_2O_3 compound.[1]

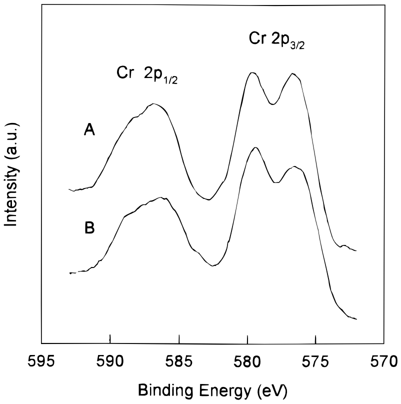


Figure 6. XPS spectra of 10 wt % CrO_3/MgO calcined at 800 °C prepared by different methods: (A) precipitation (B) impregnation.

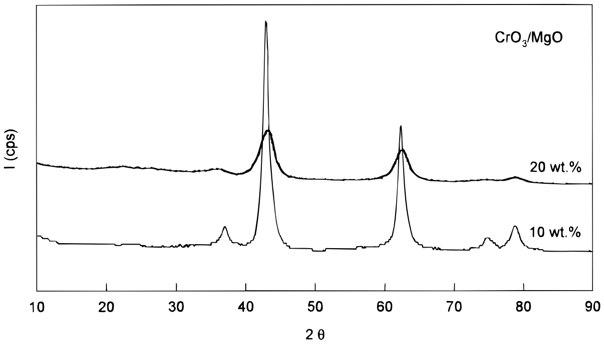


Figure 7. XRD patterns of CrO_3/MgO prepared by the precipitation method, calcined at 400 °C, as a function Cr loading.

Figure 5 shows the XPS spectra for the 5, 10, and 20 wt % Cr/MgO calcined at 400 °C for 4 h. For all samples, we obtained two peaks of similar shapes at binding energies of 579.9 and 588.9 eV, corresponding respectively to $2p_{2/3}$ and $2p_{1/2}$ of Cr(VI) species.[29]

The XPS spectra for the samples prepared by the two methods and calcined at 800 °C are also shown in Figure 6. Both Cr $2p_{3/2}$ and $2p_{1/2}$ peaks showed doublets revealing the presence of two types of chromium oxide. The better resolved doublet Cr $2p_{3/2}$ binding energies are 579.9 eV due to Cr(VI) and 576.7 eV identified as Cr(III). This result indicates that the chromium oxide exists in both Cr(VI) and Cr(III) species which have been caused by the formation of $MgCr_2O_4$ and Cr_2O_3 compounds when calcined at 800 °C.

CrO_3/MgO Prepared by Precipitation. The results of XRD analyses for CrO_3/MgO samples with different Cr loadings that had been calcined at 400 °C are shown in Figure 7. The samples with 10 and 20 wt % Cr loadings showed only the X-ray pattern of MgO, indicating again a high dispersion of chromia. None of the peaks due to chromium species were observed. The MgO loaded with 10 wt % Cr showed more intense XRD peaks, indicating better crystallinity than 20 wt % sample. When the samples were calcined at 800 °C, they showed the identical XRD results with those of the impregnated sample, namely, the formation of the $MgCr_2O_4$ structure.

The Raman spectra of chromium oxide on MgO prepared by the precipitation and calcined at 400 °C are presented in

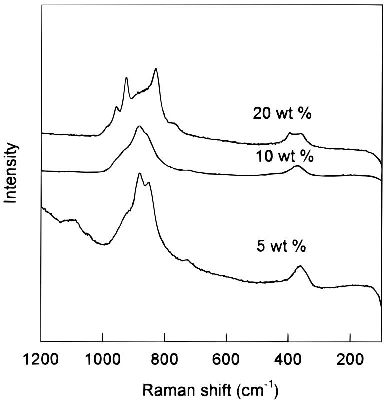


Figure 8. Raman spectra of CrO_3/MgO prepared by the precipitation method, calcined at 400 °C, as a function Cr loading.

Figure 8 as a function of chromium oxide loadings. The Raman band positions are indicative of Cr(VI) oxide. The 5 wt % Cr/MgO sample possesses main Raman bands at 880 and 360 cm^{-1}. These bands are assigned to the symmetric stretching and bending modes, respectively, and are consistent with an isolated $[CrO_4]$ surface−chromate species that is shifted due to its interaction with the oxide support from 846 to 880 cm^{-1}. As the chromium oxide loading is increased, the symmetric stretching and bending modes shift upward to 894 and 370 cm^{-1}, respectively. Even though a new band at 217 cm^{-1} due to the presence of Cr−O−Cr linkages does not appear, it is believed that the upward shift in frequency of the Raman bands is indicative of chromium oxide dimers which have also been found on alumina surfaces at high chromium oxide loadings.[1,8] The 20 wt % Cr/MgO sample shows different spectra with three more bands at 962, 930, and 848 cm^{-1}. From a comparison with the spectra of the impregnated samples in Figure 3, these extra bands are assigned to a tri- or tetrameric species. Thus, the 20 wt % Cr/MgO sample possesses mono- and polychromates. When the calcination temperature was increased to 800 °C, the precipitated sample showed Raman results identical with the impregnated sample as shown in Figure 4.

The XPS spectra for precipitated samples are in agreement with those of the impregnated samples as a function of Cr loadings. When the chromium(VI) oxide was calcined at 400 °C, the compounds do not change their oxidation state with increasing Cr loading as shown in Figure 5 for impregnated samples. On the other hand, chromium oxide calcined at 800 °C, shown in Figure 6, is partially transformed to Cr(III) due to formation of $MgCr_2O_4$ and Cr_2O_3. The Cr(III):Cr(VI) intensity ratio obtained in XPS measurements shows a higher value in precipitated samples (1.16) than in the impregnated sample (0.97).

CrO_3/MgF_2. Figure 9 shows the XRD results of 10 wt % Cr/MgF_2 samples that have been prepared by impregnation and precipitation, respectively, and calcined at 400 °C. Both samples showed the crystalline α-Cr_2O_3 phase without any other chromium structure.

The Raman spectra of impregnated and precipitated samples of 10 wt % chromium oxide on MgF_2 are shown in Figure 10. After calcination at 400 °C, Raman spectra show significantly different features between impregnated and precipitated samples. The impregnated sample exhibits Raman bands due to chromium oxygen stretch at 960, 930, and 848 cm^{-1}, which are characteristic of polychromates. Additional Raman bands due to antisymmetric and bending modes of the species are present at 770, 400, 378, and 360 cm^{-1}. Weak new bands appears at 1000−1200 and 730 cm^{-1} for the impregnated sample. Even though we failed to assign these new bands from the literature data, it could be inferred that the bands were caused by the presence of MgF_2. The Raman spectra of the precipitated sample possess intense bands at 880 and 350 cm^{-1}. These bands are assigned to the symmetric stretching and bending modes, respectively, of a tetrahedral chromium oxide species.[1]

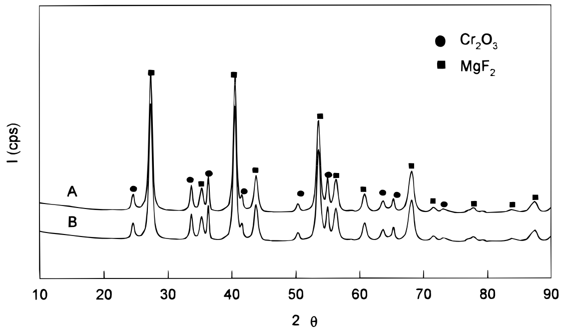


Figure 9. XRD patterns of 10 wt % CrO_3/MgF_2 calcined at 400 °C prepared by different methods: (A) precipitation (B) impregnation.

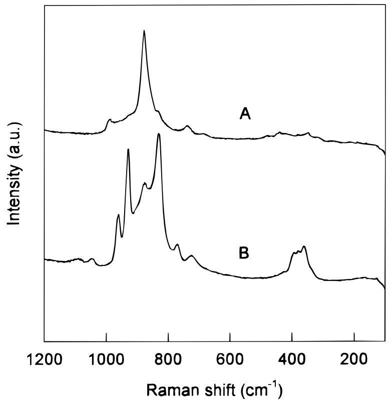


Figure 10. Raman spectra of 10 wt % CrO_3/MgF_2 calcined at 400 °C prepared by different methods: (A) precipitation (B) impregnation.

Discussion

Effects of Preparation Methods at Varying Cr Loadings. For the impregnated samples, Raman spectra reveal that the position of all bands does not vary as a function of the Cr loadings. The band positions suggest that polychromates are predominant in all samples. However, the intensity ratio of $\nu_s(Cr''O_2)$ and $\nu_s(Cr'O_3)$ $[I(960)/I(930+900)]$ decreases with increasing Cr loadings. This may possibly indicate, under the assumption of unchanging Raman scattering tensor of the different formed polymeric surface species, that the species possessing terminal CrO_3 units increase in concentration due to the formation of crystalline Cr_3O_8. The precipitated samples with 5 and 10 wt % Cr contain mostly mono- and dichromates. In addition to these two types of chromate species, polychromates were found in 20 wt % Cr/MgO.

Deo and Wachs proposed a working model to predict the molecular structure of surface metal oxide species on different oxide support under ambient conditions.[3] It was found that under ambient conditions the support surface was hydrated and the hydrated surface metal oxide structures were similar to the structures observed in aqueous solution. The hydrated surface metal oxide molecules were found to be dependent on the net pH at the point of zero surface charge (PZC) which is determined by the combined pH of the oxide support and the metal oxide overlayer. Application of this model to the chromium oxide system explains the several hydrated chromium oxide structures observed on different supports as reported in several previous works.[1,4,12] At low chromium concentrations or under basic conditions, the CrO_4^{2-} ion dominates, while in acid solutions at higher chromium concentrations, the $Cr_2O_7^{2-}$ ion is present. Under extreme conditions of strong acidity and high chromium concentrations, $Cr_3O_{10}^{2-}$ and probably $Cr_4O_{13}^{2-}$ ions are formed. In aqueous solution, the following pH-dependent equilibria can be envisaged:[33]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \tag{1}$$

$$3Cr_2O_7^{2-} + 2H^+ \rightleftharpoons 2Cr_3O_{10}^{2-} + H_2O \qquad \uparrow \ \text{pH increasing} \tag{2}$$

$$4Cr_3O_{10}^{2-} + 2H^+ \rightleftharpoons 3Cr_4O_{13}^{2-} + H_2O \tag{3}$$

The low pH of the aqueous solution shifts the equilibria of reactions 1−3 to the right.

In our Raman results, even though a very low concentration (1%) of Cr was impregnated on MgO which has pH 11 at the point of zero surface charge, the presence of polychromates was observed. The molecular structure of chromium oxide changed only a little with Cr loading. This result can be explained by the fact that $Cr(NO_3)_3$ employed as the precursor was dissolved in water and provided an extremely strong acidic solution due to HNO_3^- ($pH < 0$). Therefore, the formation of a polychromate structure in 1 wt % Cr/MgO is attributed to the acidic chromium solution employed for impregnation. Naturally, the formation of polychromates becomes more favorable with increasing Cr loadings.

The acidic chromium solution ($pH < 0$), which was also used for the preparation of the precipitated samples(5, 10, and 20 wt % Cr/MgO), may be expected to also cause a preferred formation of polychromate species as for the impregnated samples. However, samples with 5 and 10 wt % Cr contained mono- and dichromate species, respectively. At higher loadings, polychromates were also observed. Yet, the results are significantly different from those of impregnated samples which showed polychromates for all loadings from 1 wt % Cr/MgO. The first possible source of the difference in the structure of the surface chromium oxide between the precipitated and impregnated samples is the difference in the specific surface area of the supports. The values of the specific surface areas of the impregnated catalysts were in most cases close to that of the support. Yet CrOx/MgO prepared by precipitation had a much higher specific surface area (93.7 $m^2\ g^{-1}$) than the magnesia support (10 $m^2\ g^{-1}$). The treatment of magnesia with water followed by evaporation and drying under the same conditions as in the preparation of the precipitated sample showed the formation of microcrystalline $Mg(OH)_2$, as verified by XRD. Upon calcination the magnesium hydroxide decomposed into MgO, which has a higher specific surface area than the original support. This could explain the observed high specific surface area of the precipitated CrOx/MgO catalysts and the formation of mono- and dichromate structure on MgO since the structure of chromium oxide can be influenced by the surface area of support at high metal loadings.[12] Deo and Wachs reported that the preparation method (aqueous, nonaqueous, grafting) will not affect the final molecular structure of the hydrated surface metal oxide species since the molecular structures are controlled by the pH at PZC in MoO_3/TiO_2 and V_2O_5/TiO_2.[3] In our results, the influence of the preparation method can be understood by the high acidity of the preparation solution of chromium which affects the equilibria of reactions involved in the formation of chromium species and surface area of the support since the dispersion of metal oxide depends on the available surface area.

The oxidation state of Cr(VI) is maintained independent of Cr loadings. It is known that increasing chromium contents can cause decrease in the proportion of Cr(VI) due to the crystallization of Cr_2O_3 on the surface.[29,30,37] This does not seem to be the case in our case as evidenced by the absence of Cr_2O_3. During calcination not only physisorbed water is removed but also the polychromate species are anchored to the surface. The anchoring process is an acid−base type reaction: the weaker acid H_2O is replaced by the stronger $H_2Cr_2O_7$.[12,38] Hardcastle and Wachs[1] reported that the anchoring process was support-dependent. In the presence of high concentrations of surface hydroxyls, as found on the Al_2O_3 and TiO_2 supports, chromium oxide chains cannot grow very long before encountering surface hydroxyls. The surface hydroxyls appear to serve as chain terminator. Thus, Cr(VI) was more readily anchored to the surface of Al_2O_3 and TiO_2, but the Cr(VI) was partially converted to Cr_2O_3 cluster in deficiency of OH groups on silica. Therefore, we believe that the Cr(VI) is also easily anchored on MgO with enough OH groups, and then Cr(VI) is maintained independent of Cr loading. In this sense, the CrO_3/MgO sample retains its oxidation state of Cr(VI) up to the high loading of 20 wt % due to the properties of MgO having abundant OH groups.

Effects of Calcination Temperature. The effects of the calcination temperature are basically in agreement with previous observations made for different supports. All the investigated samples with highly loaded chromium oxide showed the reduction of Cr(VI) with increasing calcination temperatures.[1,26,38] The only discrepancy from prior reports in the literature has been found in the formation of $MgCr_2O_4$ as a solid-state reaction at 800 °C. This result was also confirmed by Raman and XPS. The effect of calcination temperature was the same for both preparation methods as proved by XRD, Raman spectroscopy, and XPS. However, the XPS intensity ratio of Cr(III)/Cr(VI) for the precipitated sample (1.16) is greater than that of the impregnated sample (0.97). The Raman spectra of the precipitated sample also show a higher intensity at 680 cm^{-1} relative to 880 cm^{-1} due to the $MgCr_2O_4$ structure than that of the impregnated sample. This difference can be understood as follows. The calcination results in an increased interaction between the chromate species and the support at elevated temperatures. This interaction leads to a stabilization of the chromate species by the support. Also, the chromium oxide species reacts with the support to form the $MgCr_2O_4$ structure at high temperatures (800 °C). The precipitated and impregnated samples with 10% Cr have surface areas of 93.7 and 10 m^2/g, respectively. The precipitated sample accommodates chromium species which interact directly with the support due to the higher surface area as compared to the case of the impregnated sample. Therefore, the formation of more $MgCr_2O_4$ in the precipitated sample at high temperatures causes increase in the intensity of Cr(III) in XPS and Raman spectra.

Effects of Preparation Method for MgF_2 Support. Hardcastle and Wachs[1] have reported that the dispersed chromium oxide species anchor to the oxide supports by reacting with the surface hydroxyls and that the absence of a significant population of surface hydroxyls on SiO_2 is responsible for the formation of crystalline Cr_2O_3 at low surface coverage of chromium oxide (ca. 3 wt %) on SiO_2 support, possessing a high surface area of ca. 300 m^2/g. In contrast, it is possible to disperse 13−15% CrO_3 on an Al_2O_3 support of ca. 180 m^2/g before crystalline Cr_2O_3 is formed because the Al_2O_3 support has more hydroxyl groups than SiO_2. The presence of α-Cr_2O_3 on the MgF_2 support which has a high surface area (180 m^2/g)

can be explained by the lack of significant population of surface hydroxyls on MgF_2.

A general trend of Raman spectra for the chromium structure on MgF_2 indicates that impregnated samples contain mainly polychromate species while a monochromate species is dominant in precipitated samples. Thus, even though the support MgF_2 has very acidic properties, the chromium structure is still controlled by preparation method like in the case of the MgO support. It appears that the pH of the preparation solution is more important than the acidity of the support in determining the structure of surface chromium species. As the acidic solution of chromium was precipitated by adding ammonia solution, it can be inferred that the acidic solution was neutralized by the basic solution. This precipitation process would cause the shift of equilibrium to the left. This result is in agreement with the mechanism of adsorption discussed in the previous section that is governed by the solution pH and preparation method.

Conclusion

In a series of chromium oxides supported on MgO prepared by the impregnation method, chromium oxide is present as polychrome independent of Cr loading due to a strong acidity of the $Cr(NO_3)_3$ solution employed for preparation. In the sample prepared by the precipitation method, the chromium oxide is present as monochromate at 5% Cr loading, as dichromate at 10% Cr loading, and as mono- and polychromate at 20% due to a larger surface area of the support prepared by this method. The chromium structures of impregnated and precipitated CrO_3/MgF_2 are polychromates and monochromate, respectively. The precipitation process causes the shift of equilibrium to favor monochromate due to the neutralization of acidic solution by ammonia. It is concluded that the molecular structure of chromium oxide is influenced by the solution pH and preparation method. The oxidation state of Cr(VI) on MgO is maintained independent of Cr loading due to the properties of MgO having abundant hydroxyl groups. When the 10 wt % Cr/MgO is calcined at 800 °C, $MgCr_2O_4$ and Cr_2O_3 are formed. Preferred formation of $MgCr_2O_4$ in precipitated samples relative to impregnated samples is due to the larger surface area for the former.

Acknowledgment. The authors express much appreciation to the Research Center for Catalytic Technology of POSTECH for their financial support.

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