JOURNAL OF CATALYSIS **142**, 166–171 (1993)

Surface Chemistry of Supported Chromium Oxide Catalysts

DU SOUNG KIM[1] AND ISRAEL E. WACHS[2]

Zettlemoyer Center for Surface Studies, Department of Chemical Engineering, Lehigh University,
Bethlehem, Pennsylvania 18015

Received November 2, 1992; revised February 22, 1993

A series of 1% CrO_3 supported on different oxide supports (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5, SiO_2, and MgO) was structurally characterized by Raman spectroscopy and chemically probed by methanol oxidation. The Raman results reveal that the polymeric chromium oxide species possessing two terminal Cr=O bonds preferentially exist on the Al_2O_3, TiO_2, ZrO_2, and Nb_2O_5 supports, and isolated chromate species with two Cr=O bonds predominate on the SiO_2 support. Nonstoichiometric compounds such as $Mg_x(CrO_4)_y$ are present on the MgO support due to the strong acid–base interaction of CrO_4^{2-} with MgO. The methanol oxidation reaction reveals that the reactivity of the surface chromium oxide species was primarily controlled by the specific oxide support which acts as a ligand, and not the molecular structure of the surface chromium oxide species. The selectivity of the supported chromium oxide catalysts is influenced by the acid–base characteristics of the oxide supports. © 1993 Academic Press, Inc.

INTRODUCTION

Supported chromium oxide catalysts are widely used for ethylene polymerization (Phillips catalysts: CrO_3/SiO_2) and hydrogenation/dehydrogenation of hydrocarbons (CrO_3/Al_2O_3) in the petrochemical industry. The industrial importance of chromium-based catalysts has led to a large number of fundamental studies relating their specific surface properties (*1–10*) to catalytic behavior (*1, 2, 6, 11, 12*). However, relatively few investigations have been devoted to the properties of CrO_3/support (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5, and SiO_2) catalysts for oxidation reactions (*13*). The activity and selectivity of the supported metal oxide catalysts for methanol oxidation are strongly dependent on their surface properties (*14–18*). Methanol oxidation is used as a model reaction in many studies to characterize the surface properties of catalysts (*14–16*) as well as to examine the interactions between the deposited surface oxide and the support (*17, 18*).

It is well recognized that Raman spectroscopy successfully provides the surface structural information of the supported metal oxide catalysts because of its ability to discriminate between different metal oxide species that may simultaneously be present in such catalysts (*8*). Wachs and co-workers (*8*) have proposed from Raman spectroscopic studies that the surface structures of supported metal oxides under ambient conditions, where the catalysts possess adsorbed water, resemble the metal oxide species in aqueous solution. Upon dehydration, not only does desorption of adsorbed water take place, but decomposition of the aqueous metal oxide clusters also occurs, which results in the formation of dehydrated surface metal oxide species on the support surface. The present investigation focuses on the surface structure of the supported chromium oxide catalysts on different oxide sup-

---

[1] Present address: Research and Development Division, Daelim Engineering Co., Ltd., Daelim Engineering Bldg., No. 17-5, Yoido-dong, Yongdungpo-ku, Seoul, 150-010, Korea.

[2] To whom correspondence should be addressed.

0021-9517/93 $5.00

ports under dehydrated conditions and the influence of their surface properties on the methanol oxidation reaction.

EXPERIMENTAL

A series of supported chromium oxide catalysts, containing 1% CrO_3 by weight, was prepared by the incipient-wetness impregnation method with an aqueous solution of chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, Allied Chemical Co.) (*8a*). The materials used in this study were Al_2O_3 (Harshaw, 180 m^2 g^{-1}), TiO_2 (Degussa P-25, anatase/rutile = 66/34, 55 $m^2 g^{-1}$), ZrO_2 (Degussa, 39 $m^2 g^{-1}$), and SiO_2 (Cab-O-Sil, 300 m^2 g^{-1}). The low-surface-area Nb_2O_5 support (37 m^2 g^{-1}) was obtained by calcining niobic acid (Niobia Products Co., ~110 $m^2 g^{-1}$) at 773 K for 2 h. The MgO (80 m^2 g^{-1}) support was prepared by the dehydration of magnesium hydroxide [$Mg(OH)_2$, Fluka Chemical Co.] at 973 K for 2 h. After impregnation, the wet samples were dried at room temperature for 16 h, further dried at 383–393 K for 16 h, and calcined at 773 K for 16 h.

The supported chromium oxide catalysts were structurally characterized by Raman spectroscopy, and their redox properties were probed by the methanol oxidation reaction. A sample disk of 50–100 mg was held in the quartz cell and was heated by a cylindrical heating coil at 400°C for 30 min. Oxygen gas (Linde, 99.99% purity) was introduced into the cell at a flow rate of 50–500 cm^3/min. The dehydrated Raman spectra of the supported chromium oxide catalysts were obtained with an Ar^+ ion laser (Spectra Physics Model 2020-50) delivering about 15–40 mW of incident radiation. The excitation line of the laser was 514.5 nm. The scattered radiation from the sample was directed into an optical multichannel analyzer with a photodiode array cooled thermoelectrically to 243 K (Princeton Applied Research, OMA III, Model 1463). Methanol oxidation over the 1% CrO_3/support catalysts was carried out at 503 K by using a fixed-bed tube reactor. The reactor was made of 6-mm-o.d. Pyrex glass tube held in a vertical position, and the catalyst was held in between two layers of quartz wool. About 5–20 mg of catalyst sample was employed to obtain low conversions (below 5%). Prior to the reaction, the catalyst was typically treated with flowing O_2 at 573 K for 1 h, and then the temperature was reduced to the reaction temperature. The mixture gas, $CH_3OH/O_2/He$ = 6/11/83 (mol%), flowed from the top to the bottom of the reactor, and the reaction products were analyzed by an online gas chromatograph (HP 5840A) containing two columns (Porapak R and Carbosieve S II) and two detectors (FID and TCD). Since 1% CrO_3 should be present on all the oxide supports and Raman spectroscopy revealed that only surface chromium oxide was present, the catalytic activity (TON) was calculated from the moles of methanol converted per mole of surface chromium atom per second. The catalytic activity and selectivity were measured at the initial state.

RESULTS AND DISCUSSION

The Raman spectra of the TiO_2-, ZrO_2-, and Nb_2O_5-supported chromium oxide catalysts under dehydrated conditions are presented in Fig. 1. The strong Raman features due to the TiO_2, ZrO_2, and Nb_2O_5 supports limit the collection of the data below 700 cm^{-1}. The Raman bands observed at 1010 and ~875 cm^{-1} for 1% CrO_3/TiO_2, 1010 and ~856 cm^{-1} for 1% CrO_3/ZrO_2, and ~991 and ~876 cm^{-1} for 1% CrO_3/Nb_2O_5 are attributed to the symmetric stretching modes of terminal Cr=O and O–Cr–O bonds for polymeric chromium oxide species, respectively. The CrO_3/Nb_2O_5 Raman bands increase in intensity as the CrO_3 loading is increased (*19*). The asymmetric stretching mode of the terminal Cr=O bond was not observed in this investigation because of the much weaker Raman intensity of this band relative to the symmetric stretching mode. However, the asymmetric stretching mode is observed at ~1030 cm^{-1} in the IR spectra (*8c*). The IR result supports our conclusion that essentially the same surface polymeric

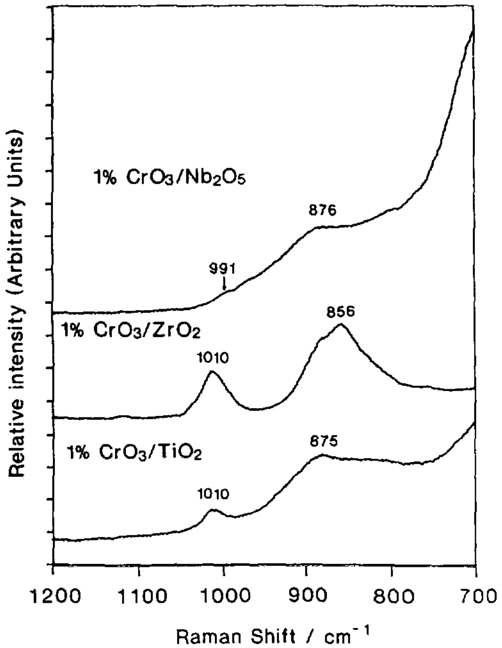

FIG. 1. Raman spectra of 1% CrO_3 supported on TiO_2, ZrO_2, and Nb_2O_5 under dehydrated conditions.

chromium oxide species possessing two terminal Cr=O bonds are present on the TiO_2, ZrO_2, and Nb_2O_5 supports.

The Raman spectra of the CrO_3/support (SiO_2, Al_2O_3, and MgO) catalysts are shown in Fig. 2. The Raman spectrum of the 1% CrO_3/SiO_2 catalyst possesses bands at 986 and $\sim$400 cm^{-1}. The weak band observed at $\sim$400 cm^{-1} is characteristic of the Raman features of the silica support (*8a*). The Raman band observed at 986 cm^{-1} is attributed to the symmetric stretching mode of the terminal Cr=O bond of the dehydrated surface chromium oxide species on the silica support (*8a*, *8c*, *8d*, *20*). The absence of the 800–900 cm^{-1} band, which is due to the O–Cr–O bond for polymeric species, indicates the isolated nature of the surface chromium oxide species on SiO_2. A similar observation is made for the silica-supported V_2O_5 (*21a*), MoO_3 (*21b*), Re_2O_7 (*8c*), and Nb_2O_5 oxide catalysts (*22*). This result is attributed to the extremely low OH density on the SiO_2 surface, as well as the silica surface chemistry (*23*). In addition, the Raman band observed at 986 cm^{-1} is consistent with the symmetric stretching mode of the terminal Cr=O bond which is observed in the CrO_2Cl_2 reference compound which possesses two terminal Cr=O bonds (*24*). Therefore, the 1% CrO_3/SiO_2 catalyst possesses an isolated chromate species with two terminal Cr=O bonds. The 1% CrO_3/Al_2O_3 catalyst reveals Raman bands at 1002, $\sim$937, 874, 765, $\sim$600, $\sim$396, and $\sim$307 cm^{-1}. The bands observed at 1002, 874, 765, $\sim$600, and $\sim$307 cm^{-1} are assigned to the ν_s (Cr=O), ν_s (O–Cr–O), ν_{as} (Cr–O–Cr), ν_s (Cr–O–Cr), and δ (O–Cr–O) of the polymeric surface chromium oxide species on Al_2O_3, respectively (*8c*, *25*). The Raman band for the Cr=O asymmetric stretching mode is not observable due to the reasons previously stated, but is present at $\sim$1020 cm^{-1} in the IR spectra (*8c*). The weak Raman bands at $\sim$937 and $\sim$396 cm^{-1} are attributed to the symmetric stretching and deformation mode of CrO_2 units which

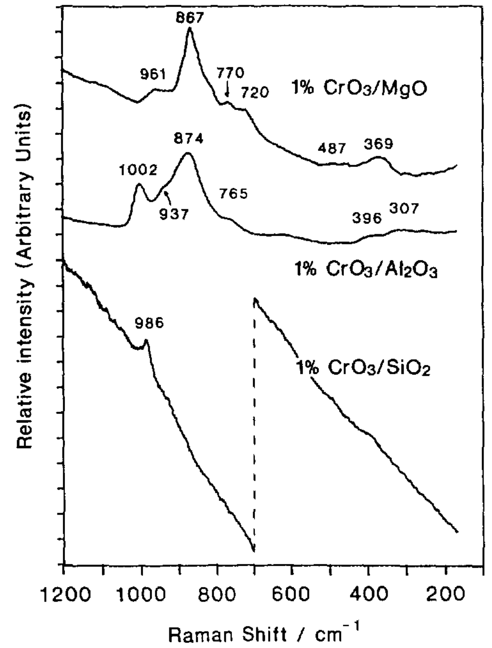

FIG. 2. Raman spectra of 1% CrO_3 supported on SiO_2, Al_2O_3, and MgO under dehydrated conditions.

terminate the surface polymeric species, respectively. The Raman result suggests that the 1% CrO_3/Al_2O_3 catalyst possesses a polymeric chromium oxide species with two terminal Cr=O bonds similar to the surface chromium oxide species on TiO_2, ZrO_2, and Nb_2O_5. The 1% CrO_3/MgO catalysts possesses a strong Raman band at 867 cm^{-1} and weak Raman bands at 961, 770, 720, 487, and 369 cm^{-1}. The band position of the terminal Cr=O bond for the 1% CrO_3/MgO catalyst is somewhat lower than that of other supported chromium oxide catalysts (986–1010 cm^{-1}). In addition, the Raman band positions for the 1% CrO_3/MgO do not correspond to the Raman bands of crystalline $MgCrO_4$ (908, 850, and 723 cm^{-1}). The very different Raman features for the 1% CrO_3/MgO catalysts are attributed to the formation of a solid solution with the MgO support due to the strong acid–base interaction of CrO_4^{2-} with MgO as well as nonstoichiometric compounds such as $Mg_x(CrO_4)_y$. A similar trend is observed for the magnesia-supported V_2O_5, MoO_3, and Re_2O_7 catalysts (*26*). Thus, similar polymerized surface chromium oxide species are present on the TiO_2, ZrO_2, Nb_2O_5, and Al_2O_3 supports, and the surface chromium oxide species on SiO_2 is isolated.

TABLE 1

Catalytic Activity for Methanol Oxidation over 1% CrO_3/Support Catalysts[a]

Support	Total rate (mmol g^{-1} h^{-1})	TON (s^{-1})
ZrO_2	466	1.3×10^0
TiO_2	108	3.0×10^{-1}
SiO_2	58	1.6×10^{-1}
MgO[b]	23	6.3×10^{-2}
Nb_2O_5[b]	21	5.8×10^{-2}
Al_2O_3[b]	1	1.6×10^{-3}

[a] Reaction temperature is 503 K; $CH_3OH/O_2/He$ = 6/11/83 (mol%). Corrected for reactivity due to the oxide support itself.

[b] The activity was calculated from sums of the redox products [HCHO, $HCOOCH_3$, and $(CH_3O)_2CH_2$].

In order to determine the influence of the support material on reactivity and selectivity of the surface chromium oxide species, the methanol oxidation reaction over 1% CrO_3 on different supports (ZrO_2, TiO_2, SiO_2, MgO, Nb_2O_5, and Al_2O_3) was carried out at 503 K. The overall activities of pure ZrO_2, TiO_2, SiO_2, MgO, and Nb_2O_5 are 7, 2, 1, 8, and 5 mmol g^{-1} h^{-1}, respectively. These reactivity values are minimal in comparison to the reactivity of the supported chromium oxide catalysts under the same reaction conditions (see Table 1). However, the Al_2O_3 support showed a very high activity (100 mmol g^{-1} h^{-1}) for methanol oxidation and 100% selectivity toward dimethyl ether, CH_3OCH_3, because of the presence of surface Lewis acid sites (*27*). Raman studies reveal that the same surface polymeric chromium oxide species possessing two terminal Cr=O bonds are present on the TiO_2, ZrO_2, Nb_2O_5, and Al_2O_3 supports. The reactivity of the surface chromium oxide species on different oxide supports was found to depend dramatically on the specific oxide support and varied by a factor of 10^3. Thus, the dramatic influence of the oxide support upon the reactivity of the supported chromium oxide catalysts is related to the surface oxide–support interactions. Similar observations were also recently made for supported vanadium oxide (*28*, *29*), molybdenum oxide (*21b*, *28*), and rhenium oxide (*28*, *30*) catalysts.

A number of earlier studies proposed that the origin of the different reactivity is due to differences in the terminal M=O bond strength which is influenced by the specific oxide supports. However, Wachs *et al.* (*28*) have recently shown that there is no relationship between the terminal M=O bond strength and its reactivity, and proposed the important role of the M–O-support bond in redox reactions. As shown in Table 1, the more reducible oxide supports (ZrO_2 and TiO_2) (*31*, *32*) possess very high reactivities, while the irreducible oxide support (Al_2O_3) (*32*) possesses a very low reactivity for methanol oxidation. The one major excep-

TABLE 2

Selectivity for Methanol Oxidation over 1% CrO_3/Support Catalysts[a]

Support	Selectivity (%)				
	HCHO	$HCOOCH_3$	$(CH_3O)_2CH_2$	CH_3OCH_3	CO + CO_2
ZrO_2	54.1	34.4	0	0	11.5
TiO_2	68.7	20.4	0	2.6	8.3
SiO_2	60.5	11.5	1.5	0.8	25.7
MgO[b]	36.2	0	0	0	63.8
Nb_2O_5[b]	50.5	0	4.2	42.6	2.7
Al_2O_3[b]	0.4	0	0	99.0	0.6

[a] Reaction temperature is 503 K; $CH_3OH/O_2/He$ = 6/11/83 (mol%).

[b] The high selectivities of CO + CO_2 for MgO and CH_3OCH_3 for Nb_2O_5 and Al_2O_3 are attributed to the supports themselves.

tion to this general trend for supported vanadium oxide (*28*, *29*), molybdenum oxide (*21b*, *28*), and rhenium oxide (*28*, *30*) catalysts is the CrO_3/SiO_2 system. The origins of this exception to the general trend are not completely understood at present, but may be due to a slightly different mechanism for this system. Consideration of the bond length also suggest that the Cr–O-support bond is expected to be more easily removed than the Cr═O bond during methanol oxidation. The results suggest that the bridging Cr–O-support bond is more important for methanol oxidation than the terminal Cr═O bond, since the Cr–O-support bond is directly influenced by the oxide support. The current findings support the conclusion by Boreskov that an increase in the energy of oxygen bonding reduces the catalytic activity for methanol oxidation (*33*).

The selectivity of the methanol oxidation reaction products over the 1% CrO_3/support catalyst is shown in Table 2. The main product for the 1% CrO_3/ZrO_2 and 1% CrO_3/TiO_2 catalysts is formaldehyde (HCHO), and methyl formate ($HCOOCH_3$) is next in abundance. The 1% CrO_3/SiO_2 gives HCHO, $HCOOCH_3$, and combustion products such as CO and CO_2. The 1% CrO_3/MgO catalyst shows high selectivity toward CO and CO_2 combustion products due to the basic property of the MgO support itself. The 1% CrO_3/Al_2O_3 and 1% CrO_3/Nb_2O_5 catalysts possess a very high selectivity toward dimethyl ether (CH_3OCH_3) due to the acidic property of the Al_2O_3 and Nb_2O_5 surfaces. The very low selectivity of redox products (HCHO or $HCOOCH_3$) over the 1% CrO_3/Al_2O_3 catalyst further reveals that the surface chromium oxide species on Al_2O_3 is not active for the methanol oxidation reaction. The present investigation shows that the specific oxide support also exerts a strong influence on the reaction product distribution during methanol oxidation.

CONCLUSION

The Raman spectroscopic studies reveal that the polymeric chromium oxide species possessing two terminal Cr═O bonds preferentially exist on the Al_2O_3, TiO_2, ZrO_2, and Nb_2O_5 supports, and isolated chromate species with two Cr═O bonds predominate on the SiO_2 support. Nonstoichiometric compounds such as $Mg_x(CrO_4)_y$ are present on the MgO support due to the strong acid–base interaction of CrO_4^{2-} with MgO. The methanol oxidation reaction reveals that the reactivity of the surface chromium oxide species was primarily controlled by the specific oxide support which acts as a ligand, and not the molecular structure of the surface chromium oxide species. The selectivity of the supported chromium oxide catalysts is influenced by the acid–base characteristics of the oxide supports.

REFERENCES

1. McDaniel, M. P., *J. Catal.* **67,** 71 (1981); **76,** 17, 29, and 37 (1982).
2. Merryfield, R., McDaniel, M. P., and Parks, G., *J. Catal.* **77,** 348 (1982); McDaniel, M. P., and Johnson, M. M., *J. Catal.* **101,** 446 (1986).
3. Hogan, J. P., *in* "Applied Industrial Catalysis" (B. E. Leach, Ed.), Academic Press, New York, 1983; *J. Polym. Sci.* **8,** 2637 (1970).
4. Hogan, J. P., and Bank, R. L. Belg. Patent 530,617 (January 24, 1985); U.S. Patent 2,825,721 (March 4, 1958).
5. Richter, M., Reich, P., and Ohlmann, G., *J. Mol. Catal.* **46,** 79 (1988).
6. Zaki, M. I., Fouad, N. E., Leyrer, J. and Knozinger, H., *Appl. Catal.* **21,** 359 (1986).
7. Fubini, B., Ghiotti, G., Stradella, L., Garrone, E., and Morterra, C., *J. Catal.* **66,** 200 (1980).
8. (a) Hardcastle, F. D., and Wachs, I. E., *J. Mol. Catal.* **46,** 173 (1988); (b) Deo, G., and Wachs, I. E., *J. Phys. Chem.* **95,** 5889 (1991); (c) Vuurman, M. A., Wachs, I. E., Stufken, D., and Oskam, O., *J. Mol. Catal.*, in press; (d) Kim, D. S., Tatibouet, J. M., and Wachs, I. E., *J. Catal.* **136,** 209 (1992).
9. Groeneveld, C., Wittgen, P. P. M. M., Van Kersbergen, A. M., Mestrom, P. L. M., Nuijiten, C. E., and Schuit, G. C. A., *J. Catal.* **59,** 153 (1979).
10. Ellison, A., *J. Chem. Soc. Faraday Trans. I* **80,** 2567 (1984).
11. Krauss, H. L., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. I, p. 207. North-Holland, Amsterdam, 1973.
12. Beck, D. D., and Lunsford, J. H., *J. Catal.* **68,** 121 (1981).
13. (a) Richter, M., and Ohlmann, G., *React. Kinet. Catal. Lett.* **29,** 211 (1985); (b) Parlitz, B., Hanke, W., Fricke, R., Richter, M., Roost, U., and Ohlmann, G., *J. Catal.* **94,** 24 (1985).
14. Segawa, K., Soeya, T., and Kim, D. S., *Sekiyu Gakkaishi* **33,** 347 (1990).
15. Louis, C., Tatibouet, J. M., and Che, M., *J. Catal.* **109,** 354 (1988).
16. Haber, J., Kozlowska, A., and Kozlowski, R., *J. Catal.* **102,** 52 (1986).
17. Roozeboom, F., Cordingleys, P. D., and Gellings, P. J., *J. Catal.* **68,** 464 (1981).
18. Deo, G., and Wachs, I. E., *J. Catal.* **129,** 307 (1991).
19. Jehng, J. M., and Wachs, I. E., *Appl. Catal.* **83,** 179 (1992).
20. (a) Wang, L., Ph.D. thesis, University of Wisconsin, 1982.
21. (a) Deo, G., PhD thesis, Lehigh University, 1992; (b) Hu, H., and Wachs, I. E., in preparation.
22. Jehng, J. M., and Wachs, I. E., *J. Phys. Chem.* **95,** 7373 (1991).
23. Kim, D. S., Segawa, K., Soeya, T., and Wachs, I. E., *J. Catal.*, in press.
24. Matters, R., *Z. Anorg. Allg. Chem.* **362,** 163 (1971).
25. Cieslak-Golonka, M., *Coord. Chem. Rev.* **109,** 233 (1991).
26. Kim, D. S., and Wachs, I. E., in preparation.
27. Jehng, J. M., and Wachs, I. E., *Catal. Today* **8,** 37 (1990).
28. Wachs, I. E., Deo, G., Kim, D. S., Vuurman, M. A., and Hu, H., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992," preprint and abstract book p. 72. Institute of Isotopes of the Hungarian Academy of Science, Budapest, 1992.
29. Deo, G., and Wachs, I. E., *J. Catal.* **129,** 307 (1991).
30. Kim, D. S., and Wachs, I. E., *J. Catal.*, in press.
31. Tauster, S. J., *Chem. Res.* **20,** 389 (1987).
32. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).
33. Boreskov, G. K., *Kinet. Katal.* **14,** 1 (1973).