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The Effect of Impurities on Chemisorption and Activity of MgO-Supported Rh

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A study has been made of the effect of the activation temperature on the properties of Rh supported on MgO of various purities. Hydrogen chemisorption, ethane hydrogenolysis, and cyclohexane dehydrogenation were used as tests for metal–support interactions. When either a 98 or 99.5% pure MgO was used as support for Rh, we observed, respectively, a 3- or 20-fold decrease in H_2 chemisorption capacity and a 3 or 5 order of magnitude suppression in ethane hydrogenolysis activity after a high temperature reduction (773 K) relative to a low temperautre reduction (523 K). The effect was reversible by oxidation at 673 K followed by reduction at low temperature in H_2 and was dependent on the loading of Rh when the dispersion of the metal was kept about constant, i.e., the lower the loading, the more profound the effect. However, little effect of reduction temperatures was observed on H_2 adsorption or ethane hydrogenolysis when a 99.999% pure MgO was used as support for Rh. The difference may be attributed to the impurities in the support, and in particular, sulfate is suspected to be the precursor of sulfide poisoning which is responsible for the apparent metal–support interaction in the Rh/MgO system.

INTRODUCTION

There has been renewed interest in the study of metal–support interaction since Tauster and co-workers (*1*, *2*) reported their observations of reduction temperature effects on chemisorption for group VIII metals supported on TiO_2 or other reducible transition metal oxides. Taüster *et al.* (*1*) ruled out explanations such as impurity effects, agglomeration, encapsulation of the metal, or incomplete reduction of the metal, etc., which may also be responsible for the observed phenomena. They explained the nature of the Strong Metal–Support Interaction (SMSI) in terms of electron transfer between the metal and reduced forms of TiO_2 or metal–metal bond formation between the noble metal and titanium cations. Similar descriptions of the origin of SMSI can be found in Refs. (*3*, *4*, *5*). Resasco and Haller (*6*) have recently proposed a model in which a reduced specie of TiO_2 migrates onto the metal particle an undergoes a localized transfer of charge t Rh after a high temperature reduction. Thi model allows an explanation of how SMS can operate on large particles and is consistent with known observations, although th model may still be subject to controvers In any case, all proposed models presum that strong metal–support interaction r quires the support to be a reducible oxid Hence, confusion has been introduced b the several reports that group VIII meta on SiO_2 (*7*), Al_2O_3 (*8–12*), and MgO (*1* exhibit a metal–support interaction qui similar to reducible oxides such as TiO although the detailed mechanisms su gested were different. For the case of Mg Adamiec *et al.* (*13*) reported results for h drogen chemisorption and transmissi electron microscopy for Pt/MgO catalyst They observed that H_2 treatment of Pt/Mg at 773 K resulted in a drastic decrease in chemisorption while the metal crystalli

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size remained constant as indicated by transmission electron microscopy. The changes brought about by high temperature in H_2 were essentially reversible by O_2 treatment. This result contradicts that reported by Tauster *et al.*, and poses the fundamental question as to whether reducibility of the support is a necessary requirement for the SMSI to occur. Although, as indicated by Imelik *et al.* (*14*), very probably metal–support interaction and metal additive effects may not be explained by one unified theory, the apparent SMSI observation for group VIII metals supported on MgO catalysts would add a further complication to our understanding of the inherent properties of the support responsible for the metal–oxide interactions.

In the course of our survey of metal–support interactions of Rh supported on different oxides, we initiated a systematic study of Rh supported on MgO with different purities to ascertain the effects of MgO impurities. Efforts have been made to characterize and to trace factors responsible for the observed apparent SMSI by H_2 chemisorption, ethane hydrogenolysis, cyclohexane dehydrogenation, and *in situ* FTIR spectroscopy. The experimental results will show that in our systems the apparent SMSI can be attributed to impurity effects, and in particular, suggest that sulfate impurity may be a precursor of sulfide poisoning.

EXPERIMENTAL

Material Used and Catalyst Preparation

The catalysts were prepared by impregnation according to the incipient wetness procedure. The magnesium oxide supports used were 98% (BET surface area 44 m^2/g), 99.5% (BET surface area 33 m^2/g, 325 mesh), and Puratronic, 99.999% purity (BET surface area 9 m^2/g), all were Alfa products (the purity is the nominal percentage claimed by the supplier). Catalysts prepared from these supports are labeled A, B, and C, respectively (see Table 1). The supports were pretreated before impregnation according to the procedure of Tauster *et al.* (*2*). Supports with known amounts of impurities were prepared by impregnation of Puratronic MgO (99.999%) with $Ca(NO_3)_2$, $Fe(NO_3)_3$, and $(NH_4)_2SO_4$; all were A. R. grade Mallinchrodt, Inc. Catalysts D, E, and F with known amounts of Ca^{2+}, Fe^{3+}, and SO_4^{2-}, respectively, were prepared as described by Fuentes and Figueras (*15*). The chemical composition of these catalysts are listed in Table 1. Ultrapure reagent grade water was used and due care was taken not to introduce any undesired impurities during the preparation. $Rh(NO_3)_3 \cdot 2H_2O$, also an Alfa product, was used as the precursor for Rh metal. The solutions were prepared by dissolving the salt in the distilled water and 2 ml of the solution per gram of support was used for impregnation. After impregnation, the catalysts were dried at room temperature in air overnight and then 4 hr in an oven at 393 K. The reduction procedure was the same for all catalysts, i.e., the catalyst was reduced in flowing H_2 at 573 K for 2 hr and then oxidized in flowing O_2 at 673 K for 2 hr. After the above treatments, the catalyst was cooled in flowing O_2 and then stored in a dessicator. Prior to hydrogen chemisorption, ethane hydrogenolysis, and cyclohexane dehydrogenation measurements, the catalyst was activated *in situ* in flowing H_2 at 523 K for 2 hr. The hydrogen used in reduction, chemisorption, and activity measurements was Airco grade 4.5, which

TABLE 1

Catalyst Designation and Description

Catalyst	MgO purity	BET surface area (m^2/g)	Rh loading (%)
A	98%	44	3
B	99.5%	33	3
C	99.999%	9	2
D	1% CaO	—	2
E	0.5% Fe^{3+}	—	2
F	0.3% SO_4^{2-}	—	2

had been further purified by passage through a palladium–silver diffusion cell. Other gases (O_2, He, and ethane) were Airco CP grade and were used as received. Cyclohexane was a reagent grade Alfa product.

The main impurities for the nominal 99.5% MgO according to elemental analysis were SiO_2, 0.2%; S (as SO_4^{2-}), 0.29%; Cu, 0.05%; Na, 0.06%; Fe, 0.03%; and CaO, 0.09%. This analysis indicates that impurities somewhat exceed those quoted by the supplier. For the ultrapure MgO, the impurities according to the certificate of analysis issued by the manufacturer are Ca, 1 ppm; Bi, Cu; Fe, Si, and Ag, each less than 1 ppm. No anionic impurities were reported.

Chemisorption and BET Measurements

The apparatus used for adsorption measurements was a conventional volumetric adsorption system. Adsorption isotherms at room temperature were measured by admitting a known quantity of gas to the adsorption cell and waiting overnight before reading the equilibrium pressure for the first point. The range of pressure used was 0–300 Torr (1 Torr = 133.3 N m^{-2}) measured with a differential pressure gauge (MKS Baratron, PDR-C-IB) provided by MKS Instruments, Inc. Prior to any measurement, the catalyst was reduced *in situ*. With the sample in flowing H_2, the temperature was raised at 5 K/min to 523 K and maintained at that level for 2 hr after which the adsorption cell was sealed and pumped at the same temperature for 5 hr. BET measurements were performed in a Perkin–Elmer sorptometer. Samples were degassed in flowing He at 523 K for 3 hr before N_2 adsorption measurements.

Activity Measurements

The activity measurements were made in a microcatalytic reactor. Both pulse and steady-state flow modes were used. The reactors are Pyrex 6-mm-o.d. glass tubing connected to stainless-steel piping by a Cajon Ultratorr union with Viton-O-rings. The reactor is suspended in an electric furnace controlled by a temperature program controller (Hewlett–Packard Model 240). Catalysts were activated *in situ* as described for H_2 chemisorption. The amount of catalyst used in the activity measurements was about 0.1 g except for cyclohexane dehydrogenation where 5 mg of catalyst diluted with 50 mg MgO (pure) was used for the measurement. The catalyst bed was 1 cm long and was preceded by a preheater section of 10 cm of 50–60 mesh glass beads which had been washed with aqua regia and heated to high temperature in air. The temperature was monitored by an iron–constantan thermocouple in contact with the reactor. For the pulse mode, the carrier gas was purified hydrogen and the hydrocarbon pulse injection was accomplished by a Carle 2015 sampling valve. The pulse size was 0.05 cm^3. The carrier flow rate was measured with a Hasting mass flowmeter at 30 cm^3/min. In the steady-state flow mode, the conditions were controlled as indicated in Ref. (*16*). Reaction products were analyzed by an on-line gas chromatograph (Varian Model 3700) with flame ionization detection following separation on a Chromosorb 104 column operated at 348 K for ethane hydrogenolysis and on a *n*-octane on Porasil column operated at 353 K for cyclohexane dehydrogenation. The details of cyclohexane dehydrogenation measurement were described elsewhere (*17*). The gas chromatograph was coupled to a Varian CDS 111 electronic integrator. The conversion levels were maintained below 5%. Rates were measured over a temperature range of 40 K and all rates were normalized to 573 K for the purpose of comparison.

In Situ FTIR

In situ FTIR transmission spectroscopy measurements were performed with a Nicolet 7000 series spectrometer using the *in situ* treatment cell constructed according to Knözinger *et al.* (*18*) modified so that it could also be used in a flow mode. Low temperature reduction (LTR, 523 K) and

TABLE 2

H_2 Chemisorption Results

Catalyst	H/Rh		
	LTR(1)	HTR	LTR(2)[a]
A	0.53	0.15	0.54
B	0.63	0.03	0.60
C	0.46	0.41	0.47
D	0.51	0.47	—
E	0.45	0.44	—
F	0.60	0.20	0.62

[a] After HTR, the catalyst was treated with O_2 at 673 K for 2 hr and then followed by LTR.

high temperature reduction (HTR, 773 K) treatments were performed for both catalyst and support (as blank) and the spectra were recorded at room temperature.

RESULTS

The room temperature hydrogen uptakes for different catalysts supported on MgO of three different impurity levels and with added impurities after various temperature treatments are presented in Table 2. Activity measurements on the same catalysts for ethane hydrogenolysis are listed in Table 3. Cyclohexane dehydrogenation, a structure-insensitive reaction, for a typical Rh supported on less pure MgO (99.5%) was also measured. In this particular system, we observed a moderate decrease (23-fold) in cyclohexane dehydrogenation activity after HTR relative to LTR.

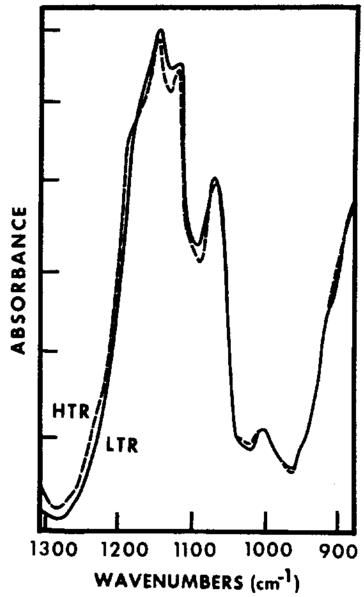

FIG. 1. Transmission infrared absorption spectra of 99.5% pure MgO after a low temperature reduction (LTR) and after a high temperature reduction (HTR).

As shown in Fig. 1, MgO support of 99.5% purity exhibited intense infrared bands at 1153, 1125, and 1071 cm^{-1} which are not affected by the temperature of reduction. These bands are attributed to sulfate impurities in accordance with the assignments of Ref. (*19*). Magnesium oxide of 99.999% purity did not exhibit any bands in the 1100-cm^{-1} frequency range (see Fig.

TABLE 3

Rates of Ethane Hydrogenolysis

Catalyst	Rate[a] (molec/surface Rh atom min)$^{-1}$			E_a (kcal mol^{-1})		
	LTR(1)	HTR	LTR(2)	LTR(1)	HTR	LTR(2)
A	63	0.019	60	43 ± 3	44 ± 3	45 ± 4
B	131	0.0003	108	49	49	43
C	73	31	70	50	44	49
D	105	74	—	48	47	—
E	111	64	—	44	46	—
F	115	0.05	196	50	51	49

[a] Rate is compared at 573 K.

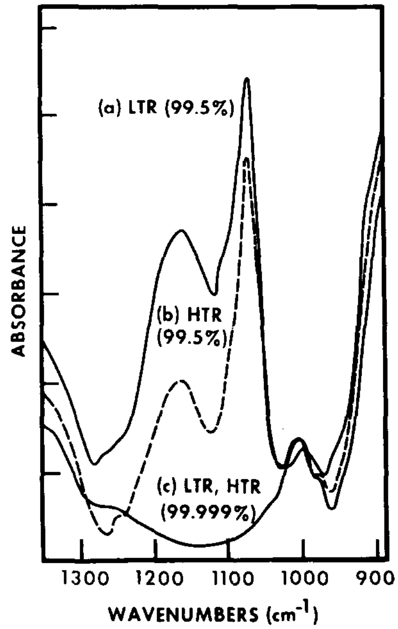

FIG. 2. Transmission infrared absorption spectra of catalyst B, 3% Rh on 99.5% MgO, compared to pure MgO. (a) Catalyst B after LTR; (b) catalyst B after HTR; and (c) 99.999% pure MgO.

2c). Ionic sulfates show only one band (ν_3) between 1130 and 1115 cm^{-1}, but if the symmetry is lowered, two or three bands appear. The triplet of bands was thus attributed to a bridged bidentate species. Sulfates of Bi, Sr, Fe(III), and Pb leave a similar set of three bands.

The 3% Rh/MgO catalyst supported on 99.5% purity magnesia showed only a doublet of bands (1167, 1071 cm^{-1}) (see Fig. 2a), indicating an increase in symmetry for the sulfate to a unidentate complex relative to the unimpregnated MgO (bidentate complex). This implies that during the impregnation process reactions between Rh cations and sulfate take place.

While the sulfate bands of the 99.5% MgO support without Rh were not affected by either LTR or HTR, for 3% Rh/MgO, catalyst B, the intensities of the sulfate bands decreased after HTR, as shown in Fig. 2b. We attribute this decrease to a partial reduction of the sulfate to sulfide which adsorbs at considerably lower wavelengths. As no reduction took place after HTR of the support alone, these results indicate that Rh plays an essential catalytic role in the reduction of the sulfate ion of impure MgO.

The effects of Rh loading on the H_2 chemisorption and ethane hydrogenolysis activity was investigated for Rh supported on MgO of 99.5 and 99.999% purity, respectively, under conditions that retained almost constant dispersion. These results are reported in Table 4. Higher Rh loadings were also attempted. However, these results are not reported because dispersion cannot be held constant, i.e., the dispersion decreased greatly when the Rh loading was higher than 6%.

When either a 98 or 99.5% pure MgO was used as support for Rh, we observed a 3- or 20-fold decrease in H_2 chemisorption, respectively, and a 3 or 5 order of magnitude suppression in ethane hydrogenolysis activity, respectively, after HTR relative to LTR

TABLE 4

Effect of Loading on the Metal–Support Interaction for Different Rh/MgO Catalysts

Catalyst	Rh loading (%)	H/Rh			Rate for ethane hydrogenolysis[a]		
		LTR(1)	HTR	LTR(2)	LTR(1)	HTR	LTR(2)
B	3	0.63	0.03	0.60	131	0.0003	108
	0.5	0.56	0.00	—	147	0.0000	—
C	2	0.46	0.41	0.47	73	31	70
	0.5	0.49	0.45	—	50	35	—

[a] In unit of molec/surface Rh atom min and normalized to 573 K.

activation (see Tables 3 and 4). In either case, the apparent activation energy for ethane hydrogenolysis remained unchanged after different temperature treatments. The effect was reversible by oxidation at 673 K followed by reduction at low temperature in H_2. In contrast, little effect of reduction was observed on H_2 adsorption or ethane hydrogenolysis when a 99.999% pure MgO was used as support for Rh. Impurities added to 99.999% pure MgO such as Ca^{2+} seem to have no large effect on the activity, Fe^{3+} has some effect, SO_4^{2-} has the largest effect. Sulfate impurity added as $(NH_4)_2SO_4$ to pure MgO did not produce as much hydrogenolysis activity suppression as experienced for the impure MgO.

When the dispersions (percentage exposed) of the metal were kept about constant, the effect of reduction temperature on H_2 adsorption and ethane hydrogenolysis was metal-loading dependent for Rh supported on a 99.5% pure MgO, i.e., the lower the loading, the more profound the effect. In contrast, again, no effect of metal loading was observed for Rh supported on ultrapure MgO (99.999%), as shown in Table 4. The rate change for cyclohexane dehydrogenation, a structure-insensitive reaction, was modest for Rh/MgO (99.5%), i.e., one order of magnitude change (a 23-fold decrease). These follow a trend in hydrogen chemisorptive capacity quite similar to that reported by Meriaudeau *et al.* (*20*).

DISCUSSION

Our results clearly emphasize that when metal–support interactions are discussed one should be very cautious to consider the possible influence of impurities. As presented in the previous section, the H_2 chemisorption capacity and ethane hydrogenolysis activity of Rh supported on less pure MgO are markedly influenced by temperature treatment in H_2, which is in agreement with the observations for group VIII metal supported on MgO systems by Adamiec *et al.* (*13*). However, no obvious effect was seen for Rh supported on ultrapure MgO, which is consistent with the report by Tauster *et al.* (*2*). Obviously, impurities were implicated here.

Before turning to the possible influence of the impurities, first consider the differences in BET surface area for different supports and other preparation procedures. As pointed out by Tauster *et al.* (*1*), the suppression of H_2 chemisorption was not dependent on the initial surface area of the TiO_2. They also reported a strong metal–support interaction over group VIII metal supported on low surface area (6.7 m^2/g) of V_2O_3 (*2*). Therefore, the different surface areas of the MgO supports may be assumed not to be critical in this study.

The preparation procedure was identical for all catalysts. All the supports used were pretreated in air (some in H_2) at a high temperature of 973 K exceeding any to which they would be subjected after introducing Rh. This treatment should structurally stabilize the supports and hence minimize the surface area reduction and the possibility of the encapsulation of the Rh. The agglomeration and incomplete reduction of the metal were ruled out by previous studies of Tauster *et al.* (*1, 2*) and Adamiec *et al.* (*13*). Therefore, one is left to consider a true metal–support interaction, or as we suggest, the possible influence of the impurities. From our H_2 chemisorption and ethane hydrogenolysis results (see Tables 2 and 3) as well as *in situ* ir spectra (see Figs. 1 and 2), we suggest that the sulfate in the support may be a poison precursor. One may argue that if all the sulfur in the 99.5% MgO acted as a poison it would correspond only to 30 mol g^{-1} MgO (and from Fig. 2, it appears that only about half of this is reduced), whereas Rh on this particular MgO sample contained 190 mol surface metal g^{-1} MgO. One must ask how such a relatively small amount of sulfur could completely poison the metal for H_2 chemisorption and ethane hydrogenolysis? This question may be answered in terms of selective poisoning and electronic effect of sulfur exerted on sites in the vicinity of S atoms. It has been suggested that the poisoning may be induced by a reduction of sulfate-containing support at a temperature of 573 K or higher (*15, 21*). When the reduction temperature is higher than 573 K, sulfur is produced which is a selective poison adsorbed predominantly on those sites responsible for hydrogenolysis (*15, 22*). This is a localized effect, but the direction of charge transfer is from metal to sulfur, just the opposite of the model suggested by Haller and co-workers for strong metal–support interaction case (*6, 17*). It should be noted here that the role of sulfur may be primarily electronic (*23*). The strong chemical bond formed with sulfur weakens the interaction of the Rh with other adsorbates and can eventually prevent the dissociation or the cracking of molecular species. In addition, certain potential sites in the vicinity of the S atom can also be deactivated by an electronic effect (weakening of the electronic density due to the electronegative character of sulfur). Therefore, often very small quantities of the poison can nearly completely deactivate a catalyst (*24*).

We propose the following interpretation for our Rh supported on the less pure MgO systems. Under H_2 atmosphere at high temperature impurities such as sulfate may migrate over the support, be reduced to sulfide, and selectively adsorbed on the sites with lower coordination number, thus poisoning these sites, and probably the sites in the vicinity of S atoms, so one observes a drastic decrease in hydrogenolysis activity after HTR. Because the loss of activity was due to the loss of sites by poisoning, no change in activation energy between HTR and LTR treatments would be expected and none was observed. LTR is unable to reduce the sulfate to sulfur (sulfide) as shown in Refs. (*15, 21, 22*). The recovery of activity by oxidation is merely the consequence of S being oxidized back to SO_4^{2-} again which may migrate back to the support. The moderate decrease in cyclohexane dehydrogenation activity can be attributed to the reaction being a structure-insensitive one. According to Leclercq *et al.* (*22, 25*), selective poisons of metallic catalysts affect differently the rates of structure-sensitive and structure-insensitive reactions. Structure-sensitive reactions such as hydrogenolysis occur only on particular ensemble sites while structure-insensitive reactions require only small ensembles or perhaps only single surface atom. Therefore, it is not surprising that the sharp decrease in hydrogenolysis activity is accompanied by only a moderate decrease in cyclohexane dehydrogenation activity when HTR is compared to LTR of Rh supported on sulfate containing MgO.

Our data in Table 4 are also interpretable by this selective poisoning model. These experimental results show that when the dispersion is kept about constant, the largest effect is seen in the case of the lowest loading for Rh supported on S-containing MgO, while no effect is seen for the pure support. From the point of view of poisoning, this is understandable. For a given amount of poison, a higher loading of the metal will allow more unpoisoned sites to remain, and hence a smaller effect of varying the activation temperature. However, one may note that from our results, it seems that sulfate may not be the only factor responsible for the phenomena (compare Tables 2 and 3). It should also be noted that there may be a combination of other factors in operation. For example, the high purity MgO has a lower defect and surface hydroxyl density, higher resistance to acid attack, etc., some of which may also have an effect on the metal–support interaction. Moreover, there are several investigations of MgO-supported metals compared to silica-supported metals where there were dramatic differences which are probably not due to impurities. Pritchard *et al.* (*26*) observed that Cu particles supported on MgO exhibited low index surface planes which SiO_2-supported Cu did not. Galvagno *et al.* (*27*) have observed a substantially different Ru–Au interaction on MgO than on SiO_2. Thus we conclude that pure MgO does not exhibit a metal–support interaction characteristic of reducible oxides such as TiO_2 but may well interact with metals in a different mode which may be catalytically significant.

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REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
2. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
3. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).
4. Horsley, J. A., *J. Amer. Chem. Soc.* **101,** 2870 (1979).
5. Bahl, M. K., Tsai, S. C., and Chung, Y. W., *Phys. Rev. B* **21,** 1344 (1980).
6. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
7. Praliauo, H., and Martin, G. A., *J. Catal.* **72,** 394 (1981).
8. Dautzenberg, F. M., and Walter, H. B. M., *J. Catal.* **51,** 26 (1978).
9. Den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53,** 116 (1978).
10. Kunimori, K., Okouchi, T., and Uchijima, T., *Chem. Lett.* 1513 (1980).
11. Kunimori, K., Ikeda, Y., Coma, M., and Uchijima, T., *J. Catal.* **79,** 185 (1983).
12. Zielinski, J., *J. Catal.* **76,** 157 (1982).
13. Adamiec, J., Wanke, S. E., Tzsche, B., and Klengler, U., *in* "Metal-Support and Metal-Additive Effects in Catalysis" (C. B. Imelik, *et al.*, Eds.), p. 77. Elsevier, Amsterdam, 1982.
14. Imelik, B., Naccache, C., Coudurier, G., Praliaud, H., Meriaudeau, P., Gallezot, P., Maring, G. A., and Vedrine, J. C., Eds., "Metal-Support and Metal-Additive Effects in Catalysis." Elsevier, Amsterdam, 1982.
15. Fuentes, S., and Figueras, F., *J. Chem. Soc. Faraday Trans. I* **74,** 174 (1978).
16. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8,** 82 (1967).
17. Haller, G. L., Resasco, D., and Rouco, A. J., *Faraday Discuss.* **72,** 109 (1982).
18. Knözinger, H., Stolz, H., Clement, HBhlG., and Meye, W., *Chem. Ing. Technol.* **42,** 548 (1970).
19. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed., p. 173. Wiley, New York, 1970.
20. Meriaudeau, P., Ellestad, H., and Naccache, C., *in* "Proceedings, 7th International Congress on Catalysis" (T. Seiyama and K. Tanbe, Eds.), Part B, p. 1464. Kodansha (Tokyo) and Elsevier, Amsterdam, 1981.
21. Fuentes, S., and Figueras, F., *J. Catal.* **54,** 397 (1978).
22. Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37,** 324 (1975).
23. Williams, D. E., Pritchard, J., and Sykes, K. W., *in* "Proceedings, 6th International Congress on Catalysis" Vol. 2, p. 417. Imperial College, London, 1976." The Chemical Society, London, 1976.
24. Hegedus, L. L., and McCabe, R. W., *Catal. Rev.—Sci. Eng.* **23**(3), 377 (1981).
25. Leclercq, G., and Boudart, M., *J. Catal.* **67,** 231 (1981).
26. Pritchard, J., Catterick, T., and Gupta, R. K., *Surf. Sci.* **53,** 1 (1975).
27. Galvagno, S., Schwank, J., Parravano, G., Garbossi, F., Marzi, A., and Tarezik, R., *J. Catal.* **69,** 283 (1981).