JOURNAL OF CATALYSIS 79, 291–297 (1983)

Water Gas Shift Reaction Catalyzed by Metal Ion-Exchanged Zeolites

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Received May 4, 1982; revised October 7, 1982

Catalytic activities of partially metal ion exchanged X- and Y-type zeolites for the water gas shift reaction have been examined in the range 473–773 K. Among the zeolites, Cu^{2+}- or Ni^{2+}-zeolites showed good performance as shift catalysts in the respective reduced states. The activity of a CuNaX zeolite prereduced at 773 K by hydrogen was comparable to that of the practical catalyst $CuO-ZnO-Cr_2O_3$. The catalytic activities of the zeolites were shown to be related to the electronegativities of metal ions.

INTRODUCTION

The water gas shift (WGS) reaction,

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

is extensively used to increase the hydrogen content of synthesis gas through the reaction of carbon monoxide with steam. The catalysts for the WGS reaction have been subjected to many theoretical and mechanistic investigations (*1*). A lot of materials are capable of catalyzing the WGS reaction, though iron- or copper-based catalysts are used almost exclusively in industry as shift catalysts which are active at temperatures above 625 K or in the range 473–573 K, respectively. Catalysts active at lower temperatures are still of interest as a result of a more favorable thermodynamic equilibrium (*2*).

Recently new types of homogeneous and heterogeneous catalysts have been produced (*3–12*). In homogeneous phase, metal carbonyls of Group VIII and VI metals are precursors of active WGS catalysts (*3, 4*). For example, King *et al.* (*3*) measured the rate of hydrogen production using iron pentacarbonyl as a catalyst in a basic methanol–water solution and observed a turnover number of 2000 mol H_2/mol $Fe(CO)_5$ per day at 453 K. On the other hand, Ru–X- (*8*), Ru–Y (*9*), Ni–Mo–Y-zeolites (*10*), and alumina-supported metals (*11*) have been reported to be active solid catalysts for the WGS reaction.

Since various transition metal cations can be exchanged for sodium ions into the zeolite structures, it is of interest to evaluate the catalytic performance of the metal ion-exchanged zeolites in the forward WGS reaction. In the present work, X- and Y-type zeolites exchanged with Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+} ions were examined. Zeolites containing Fe^{2+} and Fe^{3+} ions were also used here, but partial framework decomposition was observed by X-ray analyses after use in the catalytic reaction at elevated temperatures. This is consistent with the report by Pearce *et al.* (*13*) that iron-zeolites were unstable toward high-temperature treatment. The results concerning iron-zeolites have therefore been excluded in this paper.

EXPERIMENTAL

Transition metal ion-exchanged zeolites were prepared by conventional ion-exchange methods (*14–19*) from Linde NaY and NaX, which have compositions $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$ and $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$, respectively. The reagents used, the extents of exchange, and the colors of zeolites prepared were summarized in Table 1, in which, for example, CrNaY means a chromium ion-exchanged NaY-zeolite. The low Cr^{3+} exchange levels were

0021-9517/83/020291-07$03.00/0

intentionally selected since higher concentrations induce a notable loss of lattice crystallinity (*18–20*).

Catalytic runs were carried out in a tubular continuous-flow reactor at an atmospheric pressure. Water was supplied through a water saturator and helium was employed as a diluent gas. Standard operation conditions were as follows: amount of catalyst = 0.8 g (42–80 mesh), total flow rate = 23 cm^3 (STP) · min^{-1}, partial pressure of CO = 3.1 kPa, partial pressure of H_2O = 1.3 kPa, contact time = 2.1 g · s · cm^{-3} (STP). Reactants and products were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Over some types of zeolites the WGS reaction proceeded above ca. 473 K. A steady-state reaction was achieved for reaction times greater than about 1 h. The results at 573, 673, and 773 K are shown in Table 2. Here, a rate of 1.0 μmol · $g\text{-cat}^{-1}$ · min^{-1} for the formation of hydrogen corresponds to a conversion of 6.0% based on water. NaY and NaX exhibited small catalytic activities for the WGS reaction, while some metal ion-exchanged zeolites were active for the reaction. This indicates that the exchange of the transition metal ions into a zeolite lattice caused an appearance of catalytic performance for the WGS reaction as well as many other catalytic reactions. It is further evident that Ni^{2+}- or Cu^{2+}-zeolites show fairly high activities among the metal ion-exchanged zeolites.

TABLE 2

The WGS Reaction over Various Zeolites

Catalyst	Rate of hydrogen formation[a] (μmol · $g\text{-cat}^{-1}$ · min^{-1}) 573 K	673 K	773 K[b]
	Without prereduction of catalyst		
NaY	0.12	0.15	0.19
CrNaY	0.03	0.16	0.42
MnNaY	0.38	1.79	1.87
CoNaY	0.01	0.54	0.82
NiNaY	0.32	0.98	10.22
CuNaY	0.14	0.45	1.41
ZnNaY	0.20	0.84	1.84
NaX	0.13	0.15	0.20
CrNaX	0.21	0.23	0.26
NiNaX	0.31	1.06	10.22
CuNaX	1.60	2.68	5.53
	With prereduction of catalyst[c]		
NiNaY	0.65	3.20	10.45
CuNaY	0.56	2.33	5.45
CuNaX	5.30	7.93	8.04

[a] Experiments were performed under the standard conditions.

[b] The extent of conversion at equilibrium is 88% at 773 K under the present conditions.

[c] Catalysts were prereduced at 773 K with hydrogen (*20*).

TABLE 1

Zeolite Samples Used

Zeolite	Reagent	Exchange Level[a] (%)	Color
NaY			White
CrNaY	$CrCl_3 \cdot 6H_2O$	30	Grayish green
MnNaY	$Mn(CH_3COO)_2 \cdot 2H_2O$	54	White
CoNaY	$CoCl_2 \cdot 6H_2O$	70	Pink
NiNaY	$Ni(CH_3COO)_2 \cdot 4H_2O$	66	Yellowish green
CuNaY	$Cu(CH_3COO)_2 \cdot H_2O$	67	Blue
ZnNaY	$Zn(CH_3COO)_2 \cdot 2H_2O$	49	White
NaX			White
CrNaX	$CrCl_3 \cdot 6H_2O$	15	Grayish green
NiNaX	$Ni(CH_3COO)_2 \cdot 4H_2O$	46	Yellowish green
CuNaX	$Cu(CH_3COO)_2 \cdot H_2O$	52	Blue

[a] The extent of exchange was determined by atomic absorption spectroscopy after each sample was dissolved in concd HCl solution.

The colors of each catalyst after use in the reaction at 773 K remained unchanged except for the zeolites containing Ni^{2+} or Cu^{2+}. NiNaY and NiNaX turned black around 723 K. Since the total amount of CO and CO_2 coming out of the reactor balanced with the amount of CO fed within experimental error, the color change of the catalysts to black is probably not due to carbon deposition through the reaction, $2CO \rightarrow CO_2 + C$. The color of NiNaY was confirmed in a separate experiment to turn to blue to blue-black to black by hydrogen reduction at elevated temperatures, suggesting that the color change during the catalytic reaction is probably due to reduction of Ni^{2+}. Furthermore, as shown in Table 2, in the range 573–673 K the catalytic activity of NiNaY prereduced by hydrogen (*21*) was higher than that of NiNaY without prereduction, and at 773 K the latter was approximately equal to the former because of the reduction of Ni^{2+} by hydrogen generated in the WGS reaction. These results indicate that the reduced type of Ni-zeolite shows greater catalytic activity than the unreduced type and hence what valence state of nickel is active for the reaction is now of interest.

Electron paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) experiments have been performed for the detection of Ni^+ and Ni^0. At 773 K the NiNaY sample was outgassed in a sample tube for 1 h under a vacuum of 1.3×10^{-2} Pa, treated with oxygen of 13 kPa for 30 min, and reevacuated for 30 min. Subsequently, an EPR–FMR spectrum was determined; no signal was observed. After this sample conditioning, the zeolite was reduced by hydrogen for 10 min at 673, 723, or 773 K and subjected to EPR–FMR measurements in the presence of hydrogen. Each spectrum shows no signal at ambient temperature, though several workers have reported Ni^+ spectra (*22–24*). However, the FMR absorption due to nickel clusters ($g = 2.22$, $\Delta H = 850$ G) (*24–27*) was detected in each case upon evacuation of hydrogen at ambient temperature for only a few minutes. These findings strongly suggest the following reduction scheme.

$$\mathrm{Ni}^{2+} + \mathrm{H}_2 \rightarrow \mathrm{Ni}^0 + 2\mathrm{H}^+, \tag{1}$$

$$x\mathrm{Ni}^0 + y\mathrm{Ni}^{2+} + z\mathrm{H}_2 \rightarrow (\mathrm{Ni})_{x+y}^{2y+}(\mathrm{H}_2)_z, \tag{2}$$

$$(\mathrm{Ni})_{x+y}^{2y+}(\mathrm{H}_2)_z \xrightarrow{\text{evac.}} \mathrm{Ni}_x{}^0 + y\mathrm{Ni}^{2+} + z\mathrm{H}_2. \tag{3}$$

The formation of nickel atoms through reduction of Ni^{2+} ions located in supercages (reaction (1)) and the reaction of Ni^0 with unreduced Ni^{2+} ions to form diamagnetic nickel clusters (reaction (2)) would occur during the high-temperature reduction in the presence of hydrogen. When the sample was evacuated, disproportionation reaction (reaction (3)) would proceed to give rise to the FMR spectrum.

This scheme agrees with the experimental data that any EPR signal of Ni^+ could not be detected in the present system and that only a few minutes of evacuation resulted in the appearance of the FMR spectra. The former is probably because the migration of Ni^0 to yield clusters was easy owing to the reduction temperatures higher than those reported for the formation of Ni^+ atoms giving the EPR spectrum with $g = 2.096$ through $\mathrm{Ni}^0 + \mathrm{Ni}^{2+} \rightarrow 2\mathrm{Ni}^+$ (*22, 23*). The latter indicates that the genesis of nickel clusters does not take place during the outgassing treatment of hydrogen. Loy and Noddings (*25*) and Olivier *et al.* (*23*) have reported that Ni-zeolite samples reduced by hydrogen exhibited ferromagnetism after hydrogen was pumped off, supporting the above scheme. It is also reported by several workers that a part of Ni^{2+} remains unreduced at the present reduction temperatures (*28, 29*) and that small nickel metal clusters produced are located inside the supercages (*27, 29*). Furthermore, for example, silver metal clusters surrounded by Ag^+ ions, Ag_m^{n+} ($m > n$), have indeed been reported to be present in the supercages (*30*). On these bases, reactions (1) and (2) may be proposed and the possibility is suggested that the $(\mathrm{Ni})_{x+y}^{2y+}(\mathrm{H}_2)_z$ clusters might be generated in the WGS reaction, since hydrogen is present as one of the reaction products. It is difficult to know the values of x, y, and z in the complex, but for the sake of simplification $x = y$ will be assumed and the active valence state of nickel will formally be written Ni^+.

On Cu^{2+}-zeolites, the reduction of Cu^{2+} to Cu^+ in the working state was also observed. The color of CuNaY and CuNaX became whitish around 773 and 673 K, respectively, under the reaction conditions.

The EPR signal of Cu^{2+} ions was decreased in strength upon use in the reaction at 773 K. In addition, prereduction of CuNaY and CuNaX by hydrogen at 773 K (*21*) turned the sample color to white and resulted in the increase of catalytic activities for the reaction, as shown in Table 2 and Fig. 1. It is clear that copper exists as monovalent ions in the above prereduced copper-zeolites, based on investigations by other workers (*31, 32*) and our group (*33*). It is therefore concluded that Cu^{+} ions show higher catalytic activity than Cu^{2+} ions do. The structures of CuNaX and NiNaX were ascertained not to be changed before and after the reaction by X-ray analysis, though the X-type lattices are usually less stable than the Y-type lattices. It follows that X-zeolite is more suitable for the WGS reaction than Y since Cu^{2+} and Ni^{2+} ions could be reduced more easily in X-zeolite (*34*) and the number of metal ions exchangeable in a unit cell of X-zeolite is greater than that of Y-zeolite.

As mentioned above, the catalytic activities of Cu^{2+}- and Ni^{2+}-zeolites were improved upon the reduction to lower valence states by hydrogen produced, while the other zeolites showed no such activity change. This is consistent with the reducibilities of metal ions in a zeolite lattice. Minachev *et al.* (*35*) first reported the order of decreasing ease of reduction, $Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+}$ by X-ray photoelectron spectroscopy. In contrast, Suib *et al.* (*36*) have recently claimed that the order is $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ from their Auger study. The latter sequence appears to be correct since the order of lowest temperature for detectable reductions of metal ion zeolites was found to be $Cu^{2+} > Ni^{2+} \gg Co^{2+}$, Mn^{2+}, Zn^{2+}, Na^{+} by a temperature-programmed reduction technique using hydrogen (*37, 38*). Therefore, the catalytic activities of only Cu^{2+}- and Ni^{2+}-zeolites were improved during the reaction at elevated temperatures.

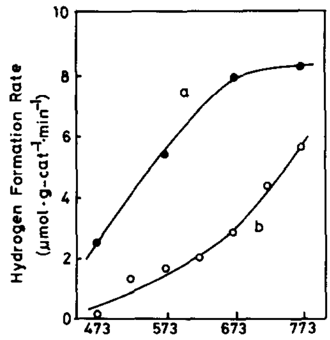

FIG. 1. The WGS reaction over CuNaX with (a) and without (b) prereduction at 773 K by hydrogen. Reaction conditions are the same as those of Table 2.

Frequent use of correlations between kinetic parameters and the physical properties of catalysts or, more desirably, the physical properties of intermediates on the surface, has been attempted. One such correlation is based on Sabatier's principle (*39*) which states that the properties of surface intermediates may qualitatively resemble the properties of bulk compounds. Accordingly, for the WGS reaction it would be reasonable to expect a relationship between the activity of the cation-exchanged zeolite catalyst and the strength of interaction of CO with the cation. In fact, it has been reported by Grenoble *et al.* (*11*) that a correlation between the heat of adsorption of CO and activity of metal catalyst supported on alumina could be constructed. Unfortunately, however, no systematic datum is available for the heat of adsorption of CO over metal ion-exchanged zeolites (*40*). Here, by using electronegativities of metal ions suggested by Tanaka and Ozaki (*41*), a relationship between the electronegativity and the zeolite's activity could be drawn (Fig. 2). The figure indicates that higher electronegativity of metal ion causes lower catalytic activity. Because carbon monoxide is one of the soft bases (*42*) and an intermediate M^{n+}–CO would be involved in the WGS reaction, if the reaction mechanism is not changed with the catalysts, one might expect that the concentration of M^{n+}–CO species will be low on highly electronegative metal ions (hard acids) due to weak interaction between metal ions and carbon monoxides, so that the activities of such metal ions will be low. It should be noted that the plots for Cu^{2+} and Ni^{2+} may not be adequate because of a possible small amount of reduction at these temperatures, though we could not observe it by color change or EPR measurements.

This discussion is strongly supported by infrared observations of other workers. Angell and Schaffer (*43*) have carried out a detailed study of carbon monoxide adsorption on a large number of divalent cation-exchanged X- and Y-zeolites. All of the zeolites only physically adsorbed carbon monoxide. Similar results have been obtained by Bregadze *et al.* (*44*). By contrast, carbon monoxide was strongly adsorbed on Ni^+-zeolites prepared by reducing Ni^{2+}-zeolite and was removed only by evacuation at 473 K (*44*). In addition, Kermarec *et al.* have very recently reported that Ni^+ ions generated by reduction with H_2 form several types of carbonyl complexes upon adsorption of carbon monoxide (*45*). Cu^+–CO complexes have also been reported to be formed upon addition of carbon monoxide at ambient temperature on reduced Cu^{2+}-zeolites (*46*). These findings conclude that carbon monoxide is more strongly adsorbed on Cu^+ or Ni^+ than on Cu^{2+} or Ni^{2+}, supporting the discussion mentioned above.

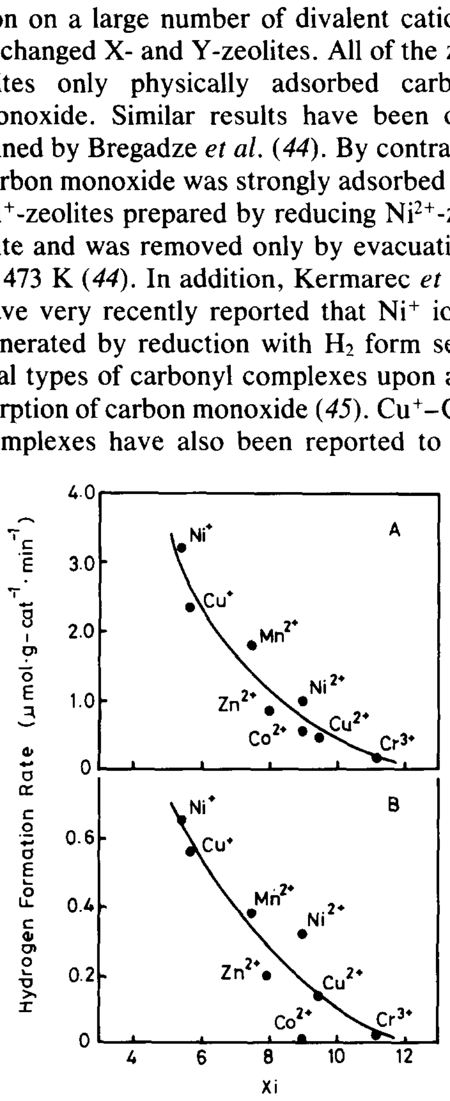

FIG. 2. Correlation between the electronegativities of metal ions (X_i) and the rates of hydrogen formation at 673 K (A) and 573 K (B).

Pressure dependencies of the WGS reaction over CuNaX prereduced at 773 K were examined in the range $P_{CO} = 3.1$–12.4 kPa and $P_{H_2O} = 1.3$–14.3 kPa. The reaction was of 0.6 order with respect to carbon monoxide and the reaction order in water is approximately 0.2. Apparently water chemisorbs strongly and almost saturates active sites under small partial pressures. Tamaru and co-workers (*47*) Amenomiya (*48*), and Verdonck *et al.* (*8*) concluded a formate ion to be an intermediate in the WGS reaction. We attempted separately to determine the surface intermediate on a CuNaY wafer which was suitable for obtaining infrared spectra in the transmission mode. However, no peaks were obtained except those due to adsorbed CO and H_2O, produced CO_2, and the CuNaY background. This would be due to small concentration of the surface species.

Finally, the activity of the prereduced CuNaX-zeolite was compared with that of a practical catalyst. $ZnO–CuO–Cr_2O_3$ was employed as the latter catalyst, which was prepared by the method of Tsuchimoto and Morita (*49*) and had a composition of 12.9 wt% CuO, 59.1 wt% ZnO, and 28.0 wt% Cr_2O_3. The formation rate of hydrogen over this catalyst was 11.5 μmol · g-cat^{-1} · min^{-1} at 673 K under the standard experimental conditions. Thus the catalytic activity of the prereduced CuNaX (7.9 μmol · g-cat^{-1} · min^{-1}) is comparable with that of the practical catalyst. This fact suggests the possibility that zeolites may be appropriate catalysts for the WGS reaction.

REFERENCES

1. Newsome, D. S., *Catal. Rev. Sci. Eng.* **21,** 275 (1980).
2. Mills, G. A., and Steffgen, F. W., *Catal. Rev. Sci. Eng.* **8,** 159 (1973).
3. King, A. D., Jr., King, R. B., and Yang, D. B., *J.*

Amer. Chem. Soc. **102,** 1028 (1980) and references therein.

4. Ford, P. C., *Acc. Chem. Res.* **14,** 31 (1981); Cole-Hamilton, D. J., *J. Chem. Soc. Chem. Commun.* 1213 (1980).
5. Giannocaro, P., Vasapollo, G., and Sacco, A., *J. Chem. Soc. Chem. Commun.*, 1136 (1980).
6. Kaneda, K., Hiraki, M., Sano, L., Imanaka, T., and Teranishi, S., *J. Mol. Catal.* **9,** 227 (1980).
7. Kambe, N., Morimoto, F., Kondo, K., and Sonoda, N., *Angew. Chem. Int. Ed. Engl.* **19,** 1007 (1980).
8. Verdonck, J. J., Jacobs, P. A., and Uytterhoeven, J. B., *J. Chem. Soc. Chem. Commun.*, 181 (1979); Verdonck, J. J., Schoonheydt, R. A., and Jacobs, P. A., *in* "Proceedings of 7th International Congress on Catalysis, 1980," p. 911. Kodansha, Tokyo, (1981).
9. Gustafson, B. L., and Lunsford, J. H., *J. Catal.* **74,** 393 (1982).
10. Lee, A. L., Wei, K. C., Lee, T. Y., and Lee, J., "Catalysis by Zeolites" (B. Imelik *et al.*, Eds.), p. 327. Elsevier, Amsterdam, 1980.
11. Grenoble, D. C., Estadt, M. M., and Ollis, D. F., *J. Catal.* **67,** 90 (1981).
12. Sato, S., and White, J. M., *J. Catal.* **69,** 128 (1981).
13. Pearce, J. R., Mortier, W. J., and Uytterhoeven, J. B., *J. Chem. Soc. Faraday Trans. 1* **77,** 937 (1981).
14. Iwamoto, M., Maruyama, K., Yamazoe, N., and Seiyama, T., *J. Phys. Chem.* **81,** 622 (1977).
15. Iwamoto, M., Yokoo, S., Sakai, K., and Kagawa, S., *J. Chem. Soc. Faraday Trans. 1* **77,** 1629 (1981).
16. Yashima, T., "Shokubai Chosei Kagaku" (A. Ozaki, Ed.), p. 67. Kodansha, Tokyo, 1980.
17. Jacobs, P. A., Tielem, M., Linart, J. P., Uytterhoeven, J. B., and Beyer, H. K., *J. Chem. Soc. Faraday Trans. 1* **72,** 2793 (1976).
18. Rubinstein, A. M., Shinkin, A. A., Loktev, M., Fedrovskaya, E. A., Bemer, H., and Vogt, F. Z., *Anorg. Allg. Chem.* **423,** 164 (1976).
19. Pearce, J. R., Sherwood, D. E., Hall, M. B., and Lunsford, J. H., *J. Phys. Chem.* **84,** 3215 (1980) and references therein.
20. Badran, A. H., Dwyer, J., Evmerides, N. P., and Manford, J. A., *Inorg. Chim. Acta* **21,** 61 (1977).
21. The prereduction of the zeolite was carried out at 773 K for 30 min by using a mixture of 10% H_2 and 90% N_2 in a flow system at atmospheric pressure.
22. Rabo, J. A., Angell, C. L., Kasai, P. H., and Shomaker, M. V., *Discuss. Faraday Soc.* **41,** 328 (1966); Kasai, P. H., Bishop, R. J., Jr., and McLeod, D., Jr., *J. Phys. Chem.* **82,** 279 (1978); Garbowski, E., and Mathieu, M. V., *Chem. Phys. Lett.* **49,** 247 (1977).
23. Olivier, D., Richard, M., Che, M., Bozon-Verduraz, F., and Clarkson, R. B., *J. Phys. Chem.* **84,** 420 (1980).
24. Che, M., Richard, M., and Olivier, D., *J. Chem. Soc. Faraday Trans. 1* **76,** 1526 (1980).
25. Loy, B. R., and Noddings, C. R., *J. Catal.* **3,** 1 (1964).
26. Misono, M., and Hall, W. K., *J. Phys. Chem.* **77,** 791 (1973).
27. Jacobs, P. A., Gilson, J., and Simoens, A. J., *J. Chem. Soc. Faraday Trans. 1* **75,** 1196 (1979).
28. Jeanjean, J., Delafoose, D., and Gallezot, P., *J. Phys. Chem.* **83,** 2761 (1979); Briend-Faure, M., Jeanjean, J., Delafosse, D., and Gallezot, P., *J. Phys. Chem.* **84,** 875 (1980); Djemel, S., Guilleux, M., Jeanjean, J., Tempere, J. F., and Delafosse, D., *J. Chem. Soc. Faraday Trans. 1* **78,** 835 (1982).
29. Jeanjean, J., Djemel, S., Guilleux, M. F., and Delafosse, D., *J. Phys. Chem.* **85,** 4145 (1981).
30. Beyer, H., Jacobs, P. A., and Uytterhoeven, J. B., *J. Chem. Soc. Faraday Trans. 1* **72,** 674 (1976); Kimm, Y., and Seff, K., *J. Amer. Chem. Soc.* **99,** 7055 (1977); Hermerschmidt, D., and Haul, R., *Ber. Bunsenges. Phys. Chem.* **84,** 902 (1980).
31. Herman, R. G., Lunsford, J. H., Beyer, H. K., Jacobs, P. A., and Uytterhoeven, J. B., *J. Phys. Chem.* **79,** 2388 (1975).
32. Gentry, S. J., Hurst, N. W., and Jones, A. J., *J. Chem. Soc. Faraday Trans. 1* **75,** 1688 (1979).
33. Iwamoto, M., Ohura, S., Furukawa, H., Nagano, H., and Kagawa, S., *Rep. Fac. Eng. Nagasaki Univ.* **18,** 89 (1982); Iwamoto, M., Ohura, S., and Kagawa, S., *J. Chem. Soc. Chem. Commun.*, 842 (1981).
34. Briend-Faure, M., Jeanjean, J., Kerwarec, M., and Delafosse, D., *J. Chem. Soc. Faraday Trans. 1* **74,** 1538 (1978).
35. Minachev, Kh. M., Antoshin, G. V., Shpiro, E. S., and Yusifov, Yu. A., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 621. The Chemical Society, London, 1977.
36. Suib, S. L., Stucky, G. D., and Blattner, R. J., *J. Catal.* **65,** 179 (1980).
37. Mahoney, F., Rudham, R., and Summers, J. V., *J. Chem. Soc. Faraday Trans. 1* **75,** 314 (1979).
38. Iwamoto, M., Ohura, S., and Kagawa, S., unpublished results.
39. Discussion of Sabatier's principle can be found in Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry and Catalytic Process," p. 206. McGraw–Hill, New York, 1979.
40. Concerning CO adsorption on metals, a detailed review has been reported by Toyoshima, I. and

Somorjai, G. A., *Catal. Rev. Sci. Eng.* **19,** 105 (1979).

41. Tanaka, K., and Ozaki, A., *J. Catal.* **8,** 1 (1967).
42. Ho, T.-S., "Hard and Soft Acids and Bases Principle in Organic Chemistry," p. 4. Academic Press, New York, 1977.
43. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **70,** 1413 (1966).
44. Bregadze, T. A., Seleznev, V. A., Kadushin, A. A., and Krylov, O. V., *Izv. Akad. Nauk SSSR Ser. Khim.*, 2701 (1973).
45. Kermarec, M., Olivier, D., Richard, M., Che, M., and Bozon-Verduraz, F., *J. Phys. Chem.* **86,** 2818 (1982).
46. Huang, Y. Y., *J. Catal.* **32,** 482 (1974).
47. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63,** 2300 (1967); Fukuda, K., Noto, Y., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63,** 3072 (1967); Tamaru, K., "Dynamic Heterogeneous Catalysis," p. 121. Academic Press, New York/London, 1978.
48. Amenomiya, Y., *J. Catal.* **55,** 205 (1978); **57,** 64 (1979).
49. Tsuchimoto, K., and Morita, Y., *Kogyo Kagaku Zasshi* **70,** 1473 (1967).