CO Adsorption on Ion-Exchanged Ru Zeolite Catalyst

An infrared study of CO adsorption on ion-exchanged RuY catalysts was carried out. At least three types of Ru sites on the reduced catlayst have been identified. It is suggested that these three types of sites are associated with (a) highly dispersed (probably atomically) Ru, (b) Ru clusters, and (c) Ru particles greater than 1.0 nm.

INTRODUCTION

Several comparative studies have shown Ru to be one of the best catalysts for the hydrogenation of CO (1), and some have found it to be the best (2–4). Obviously, one variable which may affect the activity of a particular Ru catalyst is the support. The use of zeolites for catalyst supports has become more and more widespread in the past few years as their unique properties of high surface area, molecular sieves, and catalytic activity have become recognized. Furthermore, their ion exchange capabilities have attracted considerable interest vis-à-vis the preparation of highly dispersed transition metal catalysts. It has been only relatively recently, however, that the catalytic activity of zeolite-supported Ru has begun to be studied.

Infrared spectroscopy, applied to the study of CO adsorption on a dispersed metal, provides a means to investigate support–metal interaction, particle size effects, oxidation state of surface metal atoms, nature of CO bonding to the metal atoms, and metal site distribution. To date, ir studies of CO on dispersed Ru have been for Ru supported on silica (5–10) and on alumina (5, 10–12). This paper reports on an ir study of zeolite-supported Ru.

METHODS

Zeolite-supported Ru catalysts containing 2.8–3.2 wt% Ru were prepared by ion exchange of $Ru(NH_3)_6Cl_3$ with NaY zeolite. A similar preparation scheme was also used to produce an Ru/SiO_2 catalyst.

The ion-exchanged catalysts were decomposed either under vacuum or under a flow of hydrogen. The temperature was raised slowly by 0.4°C/min to approximately 420°C where it was held for 2 hr. This slow heating schedule was necessary to prevent excessive sintering of the dispersed Ru.

EPR spectra were taken at 77°K using a Varian E9-type spectrometer.

Gas adsorption on or reaction with the dispersed catalysts was measured via a standard gas volumetry setup.

Infrared spectroscopic studies of the catalysts were carried out with a Perkin–Elmer Model 125 grating spectrometer. The pyrex ir cells were greaseless, vacuum tight, and had CaF_2 windows. Sample disks for ir investigations were prepared having diameters of 1.8 cm and weights between 10 and 20 mg. Following any treatment in CO of an ir sample, the CO pressure in the ir cell was lowered to less than 10 Torr (1 Torr = 133.3 Pa) before the spectrum was recorded to prevent interference from gaseous CO.

RESULTS

Decomposition of $ru(NH_3)_6^{3+}$ Y under vacuum to form the RuY catalyst yielded a totally dispersed Ru, as measured by H_2 adsorption, which could not be further reduced on heating in H_2 at 420°C.

The experimental results for RuY showed that this catalyst has the following attributes:

(a) a "reduced" state following decomposition of the Ru complex in which the Ru

atoms are totally dispersed, have the same stoichiometries vis-à-vis H_2 chemisorption and H_2–O_2 titration as Ru atoms on a reduced Ru metal surface, and exhibit no EPR spectrum (i.e., no Ru^{n+}, where $n = 1$, 3, 5, or 7);

(b) the multiple adsorption of CO on its surface atoms;

(c) 3 major species as detected by ir following CO adsorption at 25 or 150°C on the "reduced" catalyst (see Figs. 1a and 1b);

(d) production of the "reduced" state on heating the oxidized RuY in CO at 150°C;

(e) desorption of CO adsorbed at 150°C leaves the catalyst in a reduced state vis-à-vis H_2;

(f) no metal particles larger than 2.0 nm, as determined by electron microsocpy, even after sintering at 300°C under CO;

(g) no significant evidence of CO decom-

position on its surface at temperatures up to 300°C; and

(h) no EPR spectrum produced on heating in CO.

Following adsorption of CO at 150°C, exposure to O_2 at 25°C (Fig. 1d) resulted in a decrease or disappearance of all of the CO peaks except those at 2156 and 2100 cm^{-1}. In addition, a shoulder appeared at 2086 cm^{-1} which seemed to be associated with the other two peaks.

Preexposure of RuY to O_2 or air at 25°C followed by evacuation at 25°C for more than 1 hr yielded ir spectra upon adsorption of CO at 25°C (Fig. 2) similar to that found when CO adsorbed on Ru/SiO_2 was exposed to O_2 for a long period. These spectra were characterized by three main bands for adsorbed CO: a weak–moderate band at 2021 cm^{-1}, a very strong band at 2079, and a moderate band at 2138. These bands
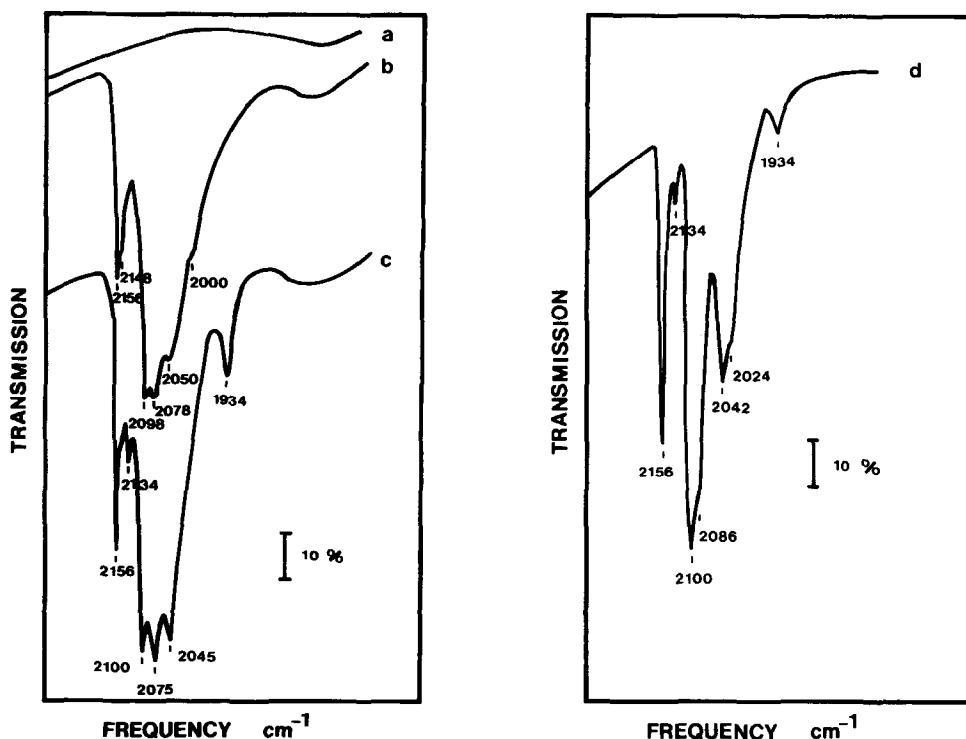

FIG. 1. Infrared spectra of RuY. (a) Following decomposition of the catalyst in flowing H_2 at 404°C and desorption at 404°C; (b) after adsorption of CO from 155 Torr CO to 25°C for 17 hr; (c) after adsorption of CO from 190 Torr CO at 150°C for 2 hr; (d) after exposure to 149 Torr O_2 at 25°C for 141 hr.
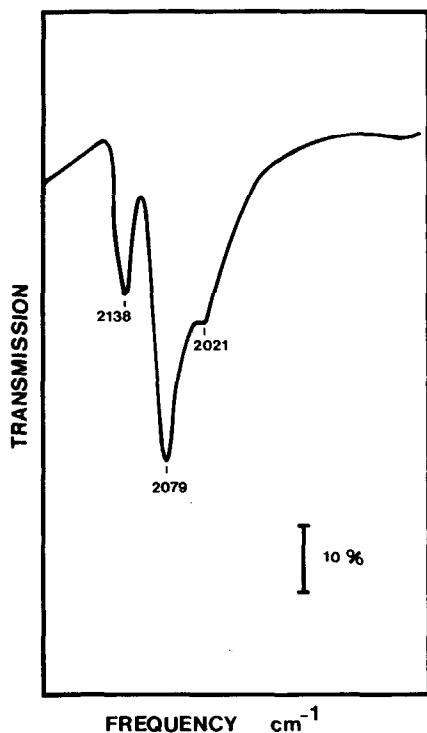
FIG. 2. Effect of preadsorption of O_2 on ir spectrum. RuY was desorbed under vacuum at 395°C for 2.5 hr, then exposed to 90 Torr of O_2 at 25°C for 17 hr, and finally evacuated at 25°C for 1.5 hr to remove physisorbed O_2. CO was then adsorbed at 25°C from 73 Torr CO for 1.5 hr.

probably correspond to CO adsorption on highly dispersed RuO_2.

DISCUSSION

The ir results reported here for CO adsorption on reduced RuY catalysts (Fig. 1) differ greatly from those for reduced Ru/SiO_2 and Ru/Al_2O_3. The results for Ru ion-exchanged into SiO_2, however, are quite similar to those reported by Davydov and Bell (9), at least for adsorption of CO on the reduced catalyst.

Adsorption of CO on either the decomposed or reduced RuY at 150°C showed the existence of at least three main species of CO adsorbed on Ru surface atoms: species A having CO vibrational bands at 2156 and 2100 cm^{-1} with perhaps a shoulder at 2086; species B having at least a band at 2075

cm^{-1}; and species C having its main band at 2045 cm^{-1} and possibly possessing also the bands at 2134 and 1934 cm^{-1}. In addition, there was often a shoulder at 2163 cm^{-1}. The results for adsorption at 25°C were essentially the same except for the apparent lack of bands at 2134 and 1934 cm^{-1} (Fig. 1).

The bands of species A were stable under O_2 at 25°C whereas all of the other bands decreased in intensity (Fig. 1d). This species did not correspond, however, to CO adsorbed on RuO_2. From gas volumetry results it is known that the totally dispersed Ru in RuY reacts with O_2 at 25°C in the ratio of 1 atom of Ru to ~2 atoms of oxygen thereby indicating the formation of RuO_2. Adsorption of CO on such supported RuO_2 gave bands at 2138, 2079, and 2021 cm^{-1} (Fig. 2).

From EPR results it is known that no significant quantities of paramagnetic Ru (that is, Ru^{1+}, Ru^{3+}, Ru^{5+}, etc.) exist following decomposition of the supported amine complex, regardless of the treatment undergone by the catalyst. Furthermore, gas volumetry results indicate that all of the Ru atoms are initially totally dispersed following decomposition and reduction, and these atoms participate in the H_2–O_2 titration reaction with the same stoichiometry as Ru atoms on the surface of large Ru metal particles. Thus, whatever species A, B, and C may be, the Ru atoms giving rise to them act as reduced atoms would. Several investigators have reported that Ru ion-exchanged with NaY zeolite can be completely reduced in H_2. Clausen and Good (13) have found using Mössbauer spectroscopy that $(Ru(NH_3)_5N_2)^{2+}$ exchanged with NaY can be completely reduced to the metallic state in flowing H_2 at 400°C. Jacobs et al. (4) and Elliott and Lunsford (14) have investigated $Ru(NH_3)^{3+}$ exchanged with NaY and have determined by gas volumetry that Ru can be reduced to the metallic state in hydrogen at temperatures as low as 300°C.

The band at 2045 cm^{-1} of species C

would seem to be the easiest of the bands to identify. Its position correlates well with that found by Brown and Gonzalez (*8*) and Davydov and Bell (*9*) for CO adsorbed on a reduced Ru metal surface in Ru/SiO_2. Whether or not the bands at 2134 and 1934 cm^{-1} also belong to species C is difficult to say. Certainly they vary in intensity with the band at 2045 cm^{-1}. Since they are not observable on adsorbing CO at 25°C but are on heating in CO at 150°C, they may be linked to the multiple adsorption of CO on the Ru surface atoms in a reduced metal surface at the higher temperature. Another possibility is that they reflect carbon deposition on the reduced Ru metal surface via decomposition/disproportionation of the CO at the higher temperature of 150°C. That disproportionation of CO can occur on supported Ru at temperatures as low as 142°C has been demonstrated by Low and Bell (*15*). In any case, species C would seem to be due to CO adsorption on Ru particles.

Species B is annihilated by exposure to O_2 and one is thus led to believe that it is probably not an ionic form of Ru. Comparison of its band(s) to those found for $Ru_3(CO)_{12}/NaY$ (Table 1) suggests the following interpretation. Species B could be considered to be an Ru carbonyl, perhaps $Ru_n(CO)_{m \cdot n}$ where n is greater than 3 and m is less than or equal to 4—that is, a carbonyl cluster compound with the Ru atoms highly coordinated with CO molecules. Having n greater than 3 would explain the

band location at 2075 cm^{-1} reather than at 2058 as found for supported $Ru_3(CO)_{12}$. It might easily have bands, other than the one at 2075 cm^{-1}, which could be hidden by the bands of the other species: a band at 2119 cm^{-1} hidden by the stronger bands at 2134 and 2100 and a band at 2040–2030 cm^{-1} appearing as, at most, a shoulder on the strong band at 2045. Thus, the Ru sites giving rise to species B are probably on small metal clusters.

Species A is more difficult to explain based on previously reported results for supported Ru. There are, however, several possible explanations for this species. The first has to do with the existence, even after reduction, of a strong support–metal interaction for certain, probably isolated, Ru atoms which produces pseudo-Ru^{2+} ions. These ions, however, would nevertheless be able to adsorb one hydrogen atom each or to react with two oxygen atoms to form RuO_2, just as in the case for Ru metal. Species A could thus correspond to an irreducible form of Ru^{2+} having multiply adsorbed CO, especially if the Ru^{2+} was also coordinated to a highly electronegative element such as oxygen. Table 1 contains results for several Ru halocarbonyls. Chloine is of course not as electronegative as oxygen; thus, substitution of oxygen in the zeolite lattice for chlorine would have the effect of decreasing the Ru–C interaction, hence strengthening the C–O bonding and resulting in even larger CO vibrational frequencies.

Another possible explanation, the retention of oxygen by very small Ru particles, as suggested by Davydov and Bell (*9*), would not seem to be the case here since it would necessitate the formation of RuO_3 or RuO_4 on interaction of the RuO or RuO_2 with O_2. This is highly unlikely at 25°C.

A third possible explanation for species A has to do with the interaction of CO with certain Ru atoms on adsorption in the absence of H_2 to produce Ru^{2+}. Desorption of the CO would then return the Ru to the reduced state. Dissociative chemisorption

TABLE 1

CO Vibrational Frequencies in Ru^{2+} Carbonyls

Carbonyl	CO frequencies[a] (cm^{-1})	Ref.
$Ru(CO)_4Cl_2$	2182w, 2132s, 2113ms, 2080s	*16*
$(Ru(CO)_3Cl_2)_2$	2145s, 2090s, 2063s(sh), 2030m(sh)	*17*
	2140s, 2092s, 2066s	*16*
$(Ru(CO)_3Cl_2)_2/NaY$[b]	2148s, 2137(sh), 2074s, 2047m(sh), 2015(sh), 1994(sh)	This paper
$Ru_3(CO)_{12}/NaY$[b]	2119w 2058s, 2025m	*18*

[a] s = strong intensity, m = medium, w = weak, (sh) = shoulder.
[b] Produced by vacuum impregnation of the support.

of CO on both supported and unsupported metals, including Ru (19), has been previously reported. In addition, dissociative chemisorption of CO followed by reassociative desorption on heating has now been shown to occur on a number of metal surfaces (20). The fact that disproportionation of CO can occur at 142°C on Ru (15) also supports this explanation.

CONCLUSIONS

Whatever the explanation for ir species A, B, and C formed by CO adsorption on reduced RuY, it is evident that these species would seem to be related to three kinds of Ru atoms: the first being highly dispersed (probably atomically), the second existing in a cluster of Ru atoms which on adsorption of CO can form a carbonyl cluster, and the third probably existing on the surface of an Ru metal particle with a diameter of 1.0 nm or more. Ione et al. (21), in a recent paper, have identified three similar types of species in an NiY catalyst: Ni²⁺ cations localized in the crystallographic centers of the zeolite, small metal clusters, and 2.0- to 5.0-nm particles external to the zeolite. Thus, RuY catalyst contains Ru sites not normally found on Al_2O_3- and SiO_2-supported Ru. This difference, without a doubt, affects their catalytic activities and selectivites.

REFERENCES

1. Dalla Betta, R. A., Piken, A. G., and Shelef, M., J. Catal. 35, 54 (1974).
2. Vannice, M. A., J. Catal. 37, 449 (1975).
3. Dalla Betta, R. A., Piken, A. G., and Shelef, M., J. Catal. 40, 173 (1975).
4. Jacobs, P. A., Nijs, H. H., Verdonck, J. J., and Uytterhoeven, J. B., Amer. Chem. Soc. Div. Petrol. Chem. Prepr. 23(2), 469 (1978).
5. Lynds, L., Spectrochim. Acta 20, 1369 (1964).
6. Guerra, C. R., and Schulman, J. H., Surface Sci. 7, 229 (1967).
7. Kobayashi, M., and Shirasaki, T., J. Catal. 28, 289 (1973).
8. Brown, M. F., and Gonzalez, R. D., J. Phys. Chem. 80, 1731 (1976).
9. Davydov, A. A., and Bell, A. T., J. Catal. 49, 332 (1977).
10. King, D. L., Amer. Chem. Soc. Div. Petrol. Chem. Prepr. 23 (no. 2), 482 (1978).
11. Unland, M. L., J. Catal. 31, 459 (1973).
12. Dalla Betta, R. A., J. Phys. Chem. 79, 2519 (1975).
13. Clausen, C. A., III, and Good, M. L., Inorg. Chem. 16, 816 (1977).
14. Elliott, D. J., and Lunsford, J. H., J. Catal. 57, 11 (1979).
15. Low, G. G., and Bell, A. T., J. Catal. 57, 397 (1979).
16. Benedetti, E., Braca, G., Sbrana, G., Salvetti, F., and Grassi, B., J. Organomet. Chem. 37, 361 (1972).
17. Johnson Matthey Chemicals catalogue.
18. Goodwin, J. G., Jr., and Naccache, C., AIChE 86th National Meeting, Houston, Texas, April 1–5, 1979, paper 72b.
19. Fuggle, J. C., Umbach, E., Feulneur, P., and Menzel, D., to be published. Cited in Joyner, R. W., J. Catal. 50, 176 (1977).
20. Joyner, R. W., and Roberts, M. W., Chem. Phys. Lett. 29, 447 (1974).
21. Ione, K. G., Romannikov, V. N., Davydov, A. A., and Orlova, L. B., J. Catal. 57, 126 (1979).

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