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Ethane Hydrogenolysis on Silica-Supported Rh–Ag Catalysts

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Several series of silica-supported Rh–Ag catalysts have been characterized by nitrogen adsorption (BET), hydrogen and carbon monoxide chemisorption, X-ray diffraction line-broadening analysis, and X-ray photoelectron spectroscopy (XPS). The two metals are shown to interact and, based on the chemisorption and XPS results, the catalysts are modeled as small crystallites of Rh with Ag deposited on the surface in a thin layer, perhaps only one atom thick. While chemisorption of hydrogen and carbon monoxide decreases as the Ag/Rh ratio increases, the rate of specific ethane hydrogenolysis is nearly constant. This is interpreted in terms of the manner in which Ag is deposited on the Rh crystallites, i.e., it forms islands of complete coverage and leaves patches of bare Rh.

INTRODUCTION

In the study of bimetallic catalysts, there is a considerable simplification in the interpretation if one of the metals is essentially inactive for the test reaction employed. Thus there are many references to studies of bimetallic catalysts of this kind (*1–3*). For reactions between hydrogen and hydrocarbons the inactive component is usually chosen from group Ib and the active component is normally from group VIII. Bimetallics between groups Ib and $VIII_3$ are by far the most popular because their adjacent position in the periodic table results in a combination of filled and nearly filled *d* bands, respectively, and, moreover, most combinations form alloys in all proportions (*1–3*).

Inclusion of inactive metal atoms in the surface of an active metal almost always lowers catalytic activity for reactions involving the rupture of C–C bonds, while little or no influence is observed for reactions involving the rupture or formation of C–H bonds. Even relatively small amounts of inactive atoms may show a large effect if they are preferentially segregated to the surface. In bimetallic systems the component with the lower heat of sublimation often accumulates in the surface and, in the case of group VIII–group Ib combinations, this component is the group Ib metal. The exception appears to be Ru–Au supported on MgO (*4*) which, due to a strong interaction between Au and MgO, results in a surface enriched in Ru instead of Au.

The existence of metal–metal interaction and its effect on catalytic activity are not limited to systems miscible in the bulk state. Work carried out on films has shown that, in systems of very limited solubility (Ir–Au (*5–7*), Rh–Ag (*8*), Rh–Au (*8*)), the addition of the group Ib metal causes a decrease in the activity for hydrogenolysis. The presence of the support does not, in general, modify this trend. The bimetallics Ir–Cu supported on Al_2O_3 (*9*), Ir–Au supported on SiO_2 (*7, 10*), Ni–Ag in zeolite (*11*), and Ru–Cu and Os–Cu supported on SiO_2 (*12*) showed the same behavior as films.

The present study of SiO_2 supported on Rh–Ag bimetallic catalysts, was initiated to extend information on the interaction of supported bimetallics which are immiscible in the bulk state. The selection of the Rh–Ag system was suggested by previous work by Anderson *et al.* (*13*) in which the authors claimed that supported Rh crystallites were covered by a layer of Ag a few atoms thick. This led to a H_2 chemisorption on the

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Rh–Ag bimetallic catalysts which was much less than that expected based on the Rh surface area calculated from X-ray diffraction line broadening. We report here results of the characterization and catalytic activity for ethane hydrogenolysis of several kinds of SiO_2-supported Rh–Ag catalysts. The effect of preparative variables such as the Rh salt used in the impregnation, the order of metal impregnation, and the kind of SiO_2 used as a support has been studied. The techniques used in the characterization of the samples were: X-ray diffraction line-broadening analysis, H_2 and CO chemisorption, N_2 adsorption (BET), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials Used and Catalyst Preparation

The catalysts were prepared by impregnation according to the incipient wetness procedure. Silica supports used were provided by Davison Chemical Company (grade 923, porous, 600 m^2/g) and Cabot Company (Cab-O-Sil HS5, nonporous, 300 m^2/g). The solutions were prepared by dissolving the salts in distilled water. The ratio of volume of impregnating solution to weight of support was 1 ml/g in the case of Davison silica and 2 ml/g when the support was Cab-O-Sil. Silver nitrate was obtained from Baker Chemical Company, $RhCl_3 \cdot 3H_2O$, and $Rh(NO_3)_3 \cdot 2H_2O$ were supplied by Fisher Scientific Company and Alfa Products, respectively. The impregnating solutions containing the cations (Rh^{3+}, Ag^+) were added to the support either simultaneously or sequentially. When the impregnation was sequential the Rh solution was put in contact with the support first, the catalyst was then dried (see procedure outlined below), and then the Ag solution was added.

After impregnation the catalysts were dried for 2 days at room temperature and then 2.5 h in air at 120°C. The dried catalysts were stored in a desiccator. The reduction procedure was as follows: approximately 1 g of dried catalyst was further dried by flowing He at 120°C for 1 h after which He was replaced by H_2 and the temperature raised at 2°C/min to 450°C. The catalyst was maintained in flowing H_2 for an additional 2 h at that temperature and then cooled in flowing He. The H_2 used in the reduction as well as in chemisorption and activity measurements was Airco grade 4.5, which had been further purified by passage through a palladium–silver diffusion cell. Other gases, He, ethane, and CO, were Airco CP grade and were used as received.

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 0–3 Torr (1 Torr = 133.3 Nm^{-2}) measured with a differential pressure gauge provided by MKS Instruments, Inc. Prior to any measurement the catalyst (approximately 0.6 g) was reduced *in situ*. With the sample in flowing H_2, the temperature was raised at 5°C/min to 300°C and maintained at that level for 1 h after which the adsorption cell was sealed and pumped at the same temperature for 5 h. An increase in temperature and time of pumping to 450°C and 8 h did not lead to a change in the amount of gas adsorbed. BET measurements were carried out in a Perkin–Elmer sorptometer. Samples were degassed in flowing He at 300°C for 3 h before N_2 adsorption measurements.

X-Ray Diffraction

The reduced catalysts were examined by X-ray diffraction using a Norelco diffractometer with $CuK\alpha$ radiation. The Ag crystallite size was estimated (when possible) from the broadening of the (111) diffraction line using the Schaerrer equation (*14*). Instrumental line broadening was determined in the angular range of interest from the width of the diffraction lines of metal foils.

X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were taken on a Hewlett–Packard 5950A spectrometer using monochromatic Al$K\alpha$ radiation. The samples were pelletized before examination and reduced *in situ* at 300°C in 0.03 Torr of H_2. Spectra were taken before and after reduction. The Rh/Si and Ag/Si intensity ratios were determined from the height of the Rh $3d_{5/2}$, Si $2p_{1/2}$, and Ag $3d_{5/2}$ lines using 20-eV sweeps. The sample was irradiated with an electron flood gun (0.3 mA, ~ 0 V) to minimize charging effects.

Activity Measurements

The activity measurements were taken with a microcatalytic pulse reactor. The reactors are Pyrex 6-mm-o.d. glass tubing connected to stainless-steel piping by a Cajon Ultra-torr 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 0.1 g. The catalyst bed, 1 cm long, was preceded by a preheater section of 3.5 g (10 cm) of 50 to 60-mesh glass beads that 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. Independent measurement of the temperature indicated a constancy within ±0.5°C. The carrier gas was purified hydrogen and the hydrocarbon pulse injection was accomplished by a Carle 2015 sampling valve. Each hydrocarbon pulse was 0.05 cm^3. The carrier flow rate was measured with a Hasting mass flowmeter at 30 cm^3/min. Analysis was performed in an on-line gas chromatograph (Varian model 3700) by flame ionization detection following separation on a Poropak Q 1-m column operated at 80°C. The conversion levels were maintained below 5%. Rates were measured at five temperatures (random order) over a 40°C range centered around 250°C. The activities are all compared at 250°C.

RESULTS

Four sets of catalysts were prepared, all were 3% by weight Rh. The Rh loading was measured by atomic absorption and found to be within 5% of the nominal value expected based on the preparation. The different Ag/Rh ratios were obtained by addition of appropriate amounts of Ag. The type of SiO_2, Rh salt used in the impregnation, the order of impregnation, and the composition of bimetallic samples are shown in Table 1. Data for H_2 and CO chemisorption are presented in Table 2.

Carbon monoxide chemisorption was very slow compared to H_2 chemisorption but the equilibrium times adopted (about 11 h for the first point, 5 h for the second, 1 h for each of the following points) were sufficient to attain equilibrium. The value for the adsorption extrapolated to zero pressure was taken as the amount corresponding to a monolayer. No adsorption on the support was observed. When values of Rh surface areas are presented they have been calculated assuming a H/Rh stoichiometry of one to one and an area of 7.6 Å^2/Rh atom. Crystallite sizes (l) were estimated from the H_2 adsorption data using the relation $l = 5/S\rho$, where S is the surface area per gram of metal and ρ is the density

TABLE 1

Catalyst Identification

Set	Support	Rh salt	Order of impreg.	Atomic percent Rh in metallic phase
A	Davison	$RhCl_3$	Sequential	20, 40, 60, 80, 100
B	Davison	$Rh(NO_3)_3$	Sequential	20, 40, 60, 80, 100
C	Davison	$Rh(NO_3)_3$	Co-impreg.	60, 70, 80, 90, 100
D	Cab-O-Sil	$Rh(NO_3)_3$	Co-impreg.	60, 70, 80, 90, 100

TABLE 2

H_2 and CO Chemisorption Results

Set	Percentage Rh	H/Rh	CO/H	Set	Percentage Rh	H/Rh	CO/H
A	100	0.69	1.10	C	100	0.89	0.96
	80	0.51	1.01		90	0.87	0.84
	60	0.58	1.07		80	0.77	0.93
	40	0.26	1.09		70	0.69	0.93
	20	0.07	—		60	0.65	0.90
B	100	0.84	1.08	D	100	0.86	0.93
	80	0.64	1.01		90	0.84	0.92
	60	0.57	0.98		80	0.73	0.98
	40	0.44	1.08		70	0.68	1.01
	20	0.36	1.10		60	0.61	1.04

of Rh. The specific H_2 adsorption of the bimetallic samples relative to the one containing pure Rh is shown in Fig. 1 as a function of group Ib/group VIII metal ratio. Results taken from the work of Anderson *et al.* (*13*) and Sinfelt (*12*) (Ru–Cu) are also included for the purpose of comparison.

Measurements of BET surface areas were carried out on sets A and C. The relative change in total surface area as a function of metal surface area is shown in Fig. 2. If the decrease in H_2 chemisorption were the result of pore blockage due to the increase in Ag content we would see a proportional decrease in total surface area. In the range of Ag/Rh atomic ratio in which we are interested (Ag/Rh < 1), no decrease in total surface area is observed. Therefore, we conclude that the decrease in H_2 chemisorption is not the result of pore blockage. X-Ray diffraction measurements were carried out primarily to determine the size of the Ag particles; results of these measurements in Table 3 show that, with the exception of set A, the particles of Ag are fairly small. The large crystals observed in set A can be attributed to the formation of AgCl which led to an increase in crystal size during the reduction process. In agreement with the apparent crystallite sizes calculated from H_2 chemisorption, see Table 4,

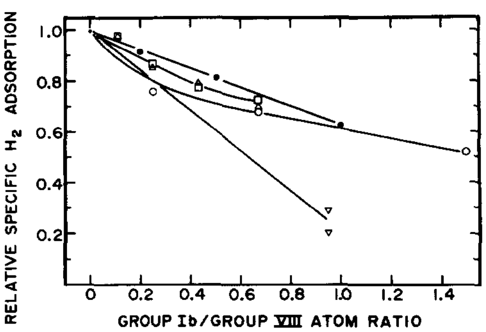

FIG. 1. The relative specific H_2 adsorption at room temperature as a function of group Ib/group VIII atom ratio for: Rh–Ag, ○ set B, □ set C, △ set D; Ru–Cu, ●, after Sinfelt, Ref. (*12*); Rh–Ag, ▽, after Anderson *et al.*, Ref. (*13*).

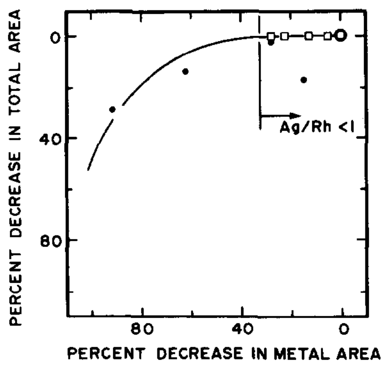

FIG. 2. Percentage decrease in total (BET) surface areas as a function of percentage decrease in Rh metal area (measured by H_2 chemisorption) for catalysts sets A, ● and C, □.

TABLE 3

X-Ray Line-Broadening Crystallite Size

Set	Percentage Rh	Rh crystal size (Å)	Ag crystal size (Å)	Set	Percentage Rh	Rh crystal size (Å)	Ag crystal size (Å)
A	100	<30	—	C	100	<30	—
	80	<30	>500		90	<30	40
	60	<30	>500		80	<30	64
	40	118	>500		70	<30	40
	20[a]				60	<30	53
					Pure Ag	—	70
B	100	<30	—	D	100	<30	<30
	80	<30	56		90	<30	<30
	60	<30	48		80	<30	<30
	40	<30	55		70	<30	<30
	20	<30	81		60	<30	<30
					Pure Ag	—	<30

[a] Not measured.

the X-ray line-broadening results indicate that Rh is highly dispersed.

Results of XPS are presented as Rh/Si and Ag/Si intensity ratios in Figs. 3 and 4, respectively. Figure 5 shows the Rh/Si XPS intensity ratio as a function of percentage exposed. The results are the average of three measurements. Due to the observation that on Davison silica support the metals are preferentially deposited on the outer portion of the particles (*15*), all samples (except those on Cab-O-Sil) were ground before pelletizing. Without this grinding there was a large scatter of metal/Si ratios for samples taken from the same batch. This was due to irreproducible breaking of particles of the samples during the process of pelletization. Two salient features of Figs. 3 and 4 are: (i) metal/Si ratios are smaller on Cab-O-Sil than on Davison silica, and (ii) the Ag/Si ratio increases with Ag content, while the Rh/Si ratio remains nearly constant.

The results of the reaction rate measurements in the pulse reactor are shown in Table 5. Figure 6 shows a comparison of the relative specific activities of the Rh–Ag and Ru–Cu systems. A measurement in a flow reactor on a sample from set C with 90% Rh at $P_{C_2H_6}$ = 0.14 atm and P_{H_2} = 0.86

TABLE 4

Rh Metal Area and Ag Coverage (Set C)

Percentage Rh	S (m^2/g)	Crystal size calc. from H_2 ads. (Å)	No. of Ag atoms covering Rh atoms / Total No. of Ag atoms	Maximum possible number of Ag layers
100	11.9	12.0	—	—
90	11.6	12.3	0.19	5.3
80	10.4	13.7	0.45	2.2
70	9.2	15.5	0.47	2.1
60	8.7	16.4	0.36	2.8

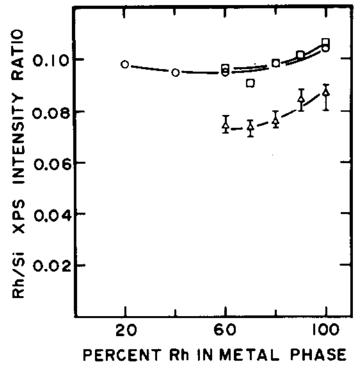

FIG. 3. XPS intensity ratio, Rh $3d_{5/2}$/Si $2p_{1/2}$, as a function of percentage Rh in the metal phase for: ○, set B; □, set C; and △, set D.

atm resulted in an activation energy of 52 kcal/mol and a reaction rate at 250°C of 4.9 × 10^{-6} mol/m^2-min compared to 5.6 × 10^{-6} mol/m^2-min for the pulse reactor. An extrapolation of the reaction rate to 250°C, $P_{C_2H_6}$ = 0.14 atm, and P_{H_2} = 0.86 atm from Sinfelt and Yates's (*16*) standard conditions of $P_{C_2H_6}$ = 0.03 atm, P_{H_2} = 0.2 atm and assuming an order of −2.2 in hydrogen, 0.8 in ethane, and E_a = 42 kcal/mol (Sinfelt and Yates's value) gave a reaction rate of 2.2 × 10^{-5} mol/m^2-min.

DISCUSSION

The first question to be asked when dealing with supported bimetallic catalysis is whether there is any interaction between the two metals. As can be seen in Table 2 the amount of H_2 and CO chemisorbed per total amount of Rh decreases systematically with the addition of Ag. Since the total BET surface area is not affected, see Fig. 2, the trivial explanation involving pore blockage by Ag can be dismissed. Thus the chemisorption results may be taken as evidence for the existence of interaction be-

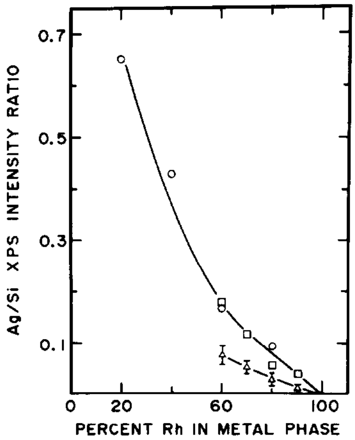

FIG. 4. XPS intensity ratios, Ag $3d_{5/2}$/Si $2p_{1/2}$, as a function of percentage Rh in the metal phase for: ○, set B; □, set C; and △, set D.

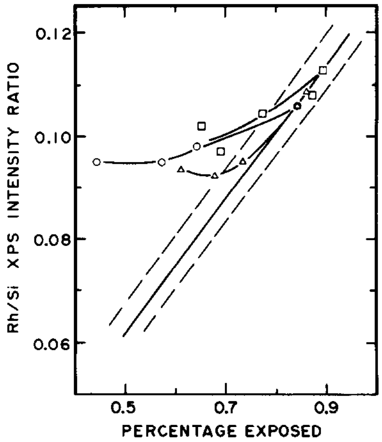

FIG. 5. XPS intensity ratio, Rh $3d_{5/2}$/Si $2p_{1/2}$, as a function of percentage exposed, H/Rh, for: ○, set B; □, set C; and △, set D. The straight line is the observed change in Rh/Si when a pure Rh catalyst, set A, was sintered in air, see Ref. (*15*). The broken lines indicate the maximum uncertainty for the XPS Rh/Si ratio as a function of percentage exposed for the sintered catalysts.

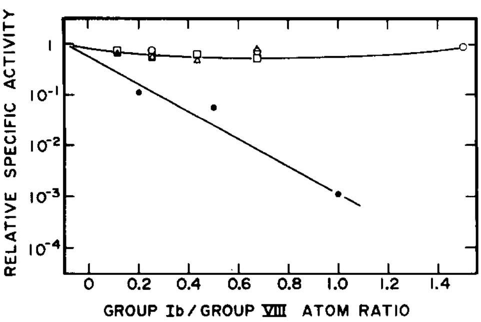

FIG. 6. The relative specific rate (normalized to H/Rh ratio) of ethane hydrogenolysis at 250°C as a function of Ag/Rh ratio: ○, set B; □, set C; and △, set D. The results of Sinfelt on Ru–Cu, Ref. (*12*), are shown for comparison, ●.

TABLE 5

Rates of Ethane Hydrogenolysis

Set	Percentage Rh	r (mol/m^2-min)	E_a (kcal/mol)	Set	Percentage Rh	r (mol/m^2-min)	E_a (kcal/mol)
A	100	2.6×10^{-5}	51	C	100	8.0×10^{-6}	52
	80	1.8×10^{-5}	49		90	5.7×10^{-6}	52
	60	1.9×10^{-5}	47		80	4.2×10^{-6}	52
	40	1.4×10^{-5}	50		70	4.6×10^{-6}	54
	20	2.8×10^{-5}	47		60	3.9×10^{-6}	52
B	100	7.9×10^{-6}	53	D	100	1.2×10^{-5}	49
	80	5.8×10^{-6}	52		90	6.9×10^{-6}	49
	60	5.4×10^{-6}	49		80	6.4×10^{-6}	51
	40	7.1×10^{-6}	52		70	5.1×10^{-6}	52
	20	8.4×10^{-6}	49		60	9.4×10^{-6}	50

tween Rh and Ag and may be rationalized by assuming an increasing coverage of Rh crystallites by Ag atoms if the Rh percentage exposed is assumed to be nearly constant throughout the range of compositions. This is in accord with the values of sublimation energies of Ag and Rh, 63.4 and 132.2 kcal/mol, respectively, which predict a large segregation of Ag to the surface.

We now consider the possibility that our underlying assumption of constant Rh dispersion is wrong, i.e., there is an increase in Rh crystallite size during the initial reduction due to the presence of Ag. X-Ray diffraction cannot be used to check this assumption because the range of possible crystallite sizes that would correspond to the observed H/Rh ratios is too small to be observed. Another technique that has been used to follow changes in dispersion is XPS (*17*). In a previous publication (*15*) we showed that a linear relationship exists between Rh/Si intensity ratio and Rh dispersion expressed as H atoms adsorbed per total number of Rh atoms (H/Rh_t). The samples used in that work were taken from set A, 100% Rh. The dispersion was changed by reducing initially in the presence of H_2O or by sintering the reduced sample in an oxygen atmosphere. One way to determine if the observed decrease in H_2 chemisorption for the bimetallic samples is due to an increase in crystallite size of Rh is to see if the relationship between measured Rh/Si XPS intensity ratios and the H/Rh_t ratios is the same as that found for the pure Rh samples with known variable dispersion. This comparison is shown in Fig. 5. The results for the Rh–Ag samples were normalized to make the results of pure Rh coincident with the full line. The fact that the changes in the XPS intensity ratios are less pronounced than the changes observed for samples with different crystallite sizes makes the possibility that Rh crystallite size increases due to the presence of Ag unlikely. Having ruled out this explanation for the observed decrease in H_2 and CO chemisorption, we are left with a model in which Rh crystallites are covered by Ag atoms.

Column 4 in Table 4 shows the fraction of Ag atoms in each sample of set C necessary to bring about the observed decrease in H_2 chemisorption, assuming one Ag atom poisons only one Rh (hydrogen chemisorption site). Column 5 in the same table shows the number of Ag layers that would be required if the remaining Ag atoms were deposited as layers on top of the first layer. It can be seen in this simple model that with the exception of the sample with 90% Rh the maximum number of layers is 2–3. Because some Ag is shown to be in a separate phase by X-ray diffraction, the simplest model which would explain our results is to assume chemisorption of Ag atoms on Rh crystallites. The photoelectrons ejected from the Rh $3d_{5/2}$ level have a mean free path of about 16 Å (*18*). Thus deposition of Ag at more than a monolayer thickness on Rh should result in considerable attenuation of the Rh signal. However, the chemisorption of Ag at monolayer thickness can explain why H_2 and CO chemisorption decreases with Ag content while the Rh/Si XPS intensity ratio remains approximately constant. The greater decrease in relative specific adsorption observed by Anderson *et al.* (*13*) (see Fig. 1) could be due to the larger size of the Rh particles in that work. It was shown in the Ru–Cu system that for the same Cu/Ru ratio the effect of Cu content on chemisorption and catalytic activity for hydrogenolysis of larger Ru particles is drastically increased (*19*). Despite the difference with previous work of Anderson *et al.* on Rh–Ag it can be seen that the decreases in relative specific adsorption with Ag content of sets B, C, and D are similar to the one observed on Ru–Cu. It should be stressed at this point that the support for catalyst set C is the same as that used by Sinfelt (*12*). It is thus surprising that the effect of group Ib metal content on the catalytic activity for ethane hydrogenolysis over Rh–Ag and Ru–Cu is very different, as can be seen in Fig. 6. A possible explanation for the smaller effect of Ag on the catalytic activity of Rh relative to the Ru/Cu system could be based on the size of the ensemble of atoms constituting the active site on Rh. If the ensemble of atoms were smaller for Rh than for Ru the effect of addition of an inert metal would be smaller on Rh. To the best of our knowledge, no experimental evidence that shows a larger active site for ethane hydrogenolysis on Ru compared to Rh exists but the contrary is suggested by Bond (*20*). Bond has used the compensation effect correlation to extract a relative order of magnitude for the ethane hydrogenolysis site density which suggests that the site atom density is greater on Ru than on Rh. This may be interpreted as a smaller number of atoms required to constitute an active site on Ru relative to Rh. It should be pointed out that Foger and Anderson have recently studied Ir–Au, a system analogous to Rh–Ag (*10*). They believe that hydrogenolysis of the C_2 unit requires more than one surface Ir atom but suggest that it may require as few as two adjacent atoms to define a critical reactant site surrounded by a secondary site, e.g., that portion of the site that adsorbs hydrogen (*21*).

A second, and more plausible explanation for the difference in catalytic behavior is based on the manner in which the group Ib metal is distributed on the surface of Rh or Ru, i.e., the distribution of Cu on Ru may be more uniform than the distribution of Ag on Rh. In other words, Ag atoms tend to cluster, forming "islands" on the surface, and this leads to a much smaller effect on the specific activity for ethane hydrogenolysis. A recent work involving Cu deposition on Ru (0001), a model catalyst, showed that up to a coverage of 60%, Cu is randomly distributed in the surface (*22*). This is the result of a higher Cu–Ru bond energy than Cu–Cu bond energy (84 kcal/mol compared to 80 kcal/mol). Unpublished results of White indicate the reverse is true for Ag–Rh, i.e., the Ag–Ag bond energy is greater than the Ag–Rh bond energy (*23*). In agreement with our model, White finds that H_2 chemisorption decreases linearly with Ag coverage of Rh (111). This too contrasts with behavior of Cu on Ru (0001) reported by Christmann *et al.* (*22*).

Infrared analysis of CO adsorption is a technique that can be used to determine the way group Ib metals distribute on group VIII metal surfaces. The addition of Ag to Pd (*24*) and Cu to Rh (*25*) led to a total suppression of the band due to CO adsorbed in the bridge form relative to linear or gem dicarbonyl, $Rh(CO)_2$, forms. It may be inferred that Ag atoms on Pd and Cu atoms on Rh surfaces are well interdispersed, otherwise there would be a proportional decrease in intensity of all bands. Studies of this kind on our Rh–Ag catalysts are in progress.

CONCLUSIONS

The main conclusions that can be drawn from the present work are:

(1) the metals Rh and Ag which are practically immiscible in the bulk form bimetallic clusters when highly dispersed on high-area SiO_2 support;

(2) the layer of Ag atoms on top of Rh is very thin, probably one atom thick, as proposed on the basis of previous work (*13*);

(3) atoms of Ag tend to cluster into islands on the surface of Rh as opposed to Cu on Ru which appears to be randomly dispersed;

(4) the texture of the silica support (Davison and Cab-O-Sil, porous and nonporous, respectively) does not affect the Rh–Ag interaction. The anion of the Rh salt (Cl or NO_3) has a small effect on activity (*15*).

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REFERENCES

1. Ponec, V., *Catal. Rev.* **11**(1), 41 (1975).
2. Sachtler, W. M. H., and Van Santen, R. A., *in* "Advances in Catalysis and Related Subjects," Vol. 26, p. 69. Academic Press, New York/London, 1976.
3. Moss, R. L., *in* "Catalysis" (C. Kemball, Ed.), Vol. 1, p. 37. The Chemical Society, London, 1977.
4. Galvagno, S., Schwank, J., and Parravano, G., *J. Catal.* **61**, 223 (1980).
5. Plunkett, T. J., and Clarke, J. K. A., *J. Catal.* **35**, 330 (1974).
6. Hagen, D. I., and Somorjai, G. A., *J. Catal.* **41**, 466 (1976).
7. Karpinski, Z., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **71**, 2310 (1975).
8. Péter, A., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **72**, 1201 (1976).
9. Brunelle, J. P., Montarnal, R. E., and Sugier, A. A., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 84. The Chemical Society, London, 1977.
10. Foger, K., and Anderson, J. R., *J. Catal.* **64**, 448 (1980).
11. Reman, W. G., Ali, A. H., and Schuitt, G. C. A., *J. Catal.* **20**, 374 (1971).
12. Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
13. Anderson, J. H., Jr., Conn, P. J. and Branderberger, S. G., *J. Catal.* **16**, 404 (1970).
14. Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials." Wiley, New York, 1974.
15. Rouco, A. J., and Haller, G. L., *in* "Proceedings, 7° Simposio Iberoamericano de Catálisis La Plata, Rep. Argentina, 1980.
16. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).
17. Brinen, J. S., Schmitt, J. L., Doughman, W. R., Achorn, P. J., Siegel, L. A., and Delgass, W. N., *J. Catal.* **40**, 295 (1975).
18. Brundle, C. R. J., *Vac. Sci. Technol.* **11**(1), 212 (1974).
19. Sinfelt, J. H., Lam, Y. L., Cusumano, J. A., and Barnett, A. E., *J. Catal.* **42**, 227 (1976).
20. Bond, G. C., *in* "The Physical Basis for Heterogeneous Catalysis" (E. Draughlis and R. I. Jaffee, Eds.). Plenum, New York, 1974.
21. Anderson, J. R., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.* **26**, 361 (1981).
22. Christmann, K., Ertl, G., and Shimizu, H., *J. Catal.* **61**, 397 (1980).
23. White, J. M., private communication.
24. Primet, M., Mathiew, M. V., and Sachtler, W. M. H., *J. Catal.* **44**, 324 (1976).
25. Bianchi, D., Belaid, A., Hoang-Van, C., Ghorbel, A., and Teichner, S. J., *C.R. Acad. Sci. Paris Sér. C* **290**, 61 (1980).