JOURNAL OF CATALYSIS 59, 340-356 (1979)

Infrared and ESCA Studies of a Heterogenized Rhodium Carbonylation Catalyst

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Received June 15, 1978; revised February 12, 1979

A heterogeneous catalyst (RhX with 0.6% Rh) obtained by the interaction of 13X molecular sieve zeolite (NaX) and rhodium trichloride, and active in the carbonylation of methanol to acetic acid, has been examined spectroscopically using ir and ESCA. Interaction of the catalyst with carbon monoxide alone at 373 to 433 K produces a multicarbonyl complex, $Rh(CO)_x$, where x is probably 2. In the additional presence of methyl iodide a rhodium–acyl unit is obtained. Evidence is presented which suggests that this acyl complex can undergo conversion to an acetate species on the surface. The ESCA study additionally reveals that the rhodium which interacts with carbon monoxide is in an oxidized state, but that rhodium trichloride itself is not present in the surface of the catalyst. It is suggested that the zeolite lattice may have a very specific action in assisting the production of rhodium centers which are active in carbonylation. Quantitative evaluation of the spectroscopic data suggests that of the *total* (*bulk*) rhodium in RhX only ~1% may be able to interact with carbon monoxide, but that on the other hand full participation of all the *surface* rhodium available does occur.

INTRODUCTION

Heterogeneous rhodium catalysts possessing high activity and high selectivity for the carbonylation of methanol may be obtained by incorporation of rhodium trichloride into a molecular sieve zeolite (*1–4*). Results of kinetic studies suggest that the catalytic behavior of heterogenized rhodium parallels that displayed by homogeneous catalysts (*5, 6*). A basis for understanding this similarity is provided by infrared spectroscopic observations which have revealed that carbon monoxide and methyl iodide interact on RhX to produce an acetylrhodium complex (*7*). The infrared bands are essentially identical in position and manner of generation to those found for the analogous reaction with rhodium trichloride in solution (*8*). In both cases reaction with carbon monoxide alone results in the formation of a carbonylrhodium unit (*7, 8*).

In order to characterize further the surface chemistry of RhX the infrared investigations have been extended and augmented by an ESCA examination. It is felt that the use of these two spectroscopic techniques in close conjunction has a special attraction in studying surface processes. The complementary nature of the two methods is exemplified by the results reported here.

EXPERIMENTAL

RhX was prepared from Linde molecular sieve zeolite Type 13X and rhodium tri-

0021-9517/79/120340-17$02.00/0

chloride as previously described (*3*). The catalyst contained 0.6% rhodium by weight. Some results were obtained using rhodium trichloride supported on silica (Degussa 200) at a similar metal content. Carbon monoxide, methyl iodide, and acetic acid were carefully purified before use.

For the infrared studies a cell of construction similar to that described elsewhere (*9*) was employed with a grating spectrometer (Perkin–Elmer 177). Self-supporting disks of RhX and NaX were formed by application of a static load at a pressure of 75 MPa. The "thickness" of the disks was 25 mg cm^{-2}. For silica-supported samples the pressure used was about 10 MPa, and the disks had an identical "thickness." A high degree of attenuation of the reference beam was required, particularly for the zeolite disks due to losses in radiation by scattering. The nominal spectral slit width used was about 3 to 4 cm^{-1} throughout the range of interest. All spectra were recorded for a sample temperature of 333 K.

The ESCA studies were performed at room temperature on an AEI ES 200B electron spectrometer equipped with a hemispherical electrostatic analyzer, which was run in the fixed retardation mode. Oil diffusion pumps fitted with cold traps produced a vacuum between 10^{-5} and 10^{-7} Pa depending on the degassing rate from the samples. All spectra presented here were obtained with Al$K\alpha$ radiation (1486.6 eV). Maximal slitwidths (200 thou) were chosen to enhance the sensitivity. The full width at half maximum (FWHM) of the Au $4f_{7/2}$ line was 1.8 eV. The instrument was calibrated as described elsewhere (*10*). Sample charging was corrected for by placing the C 1s line of the carbon contamination at 285 eV.

The sample treatment was performed in a preparation chamber connected to the electron spectrometer. The adsorption of CO and CH_3I was carried out by keeping the sample at 433 K and leaking the gas into the chamber until the desired pressure was obtained. The sample heater was turned off after the requisite time had elapsed, and when at room temperature the chamber was pumped down to vacuum. After a fast pressure decrease to about 10^{-4} Pa a much slower decrease to 10^{-7} Pa was noted, during which the spectra were obtained. Samples not treated in the preparation chamber were studied at 10°C by use of liquid nitrogen cooling.

Curve deconvolution of the spectra was performed on a HP 9100B desk calculator with a 9125A plotter by adjusting the positions, half-widths, and intensities of the Gaussian-shaped components until a correct fit was obtained.

For the quantitative estimations the peak area above the base line was measured with a planimeter. This area was corrected with the counting rate setting and the elemental sensitivity factor for photoemission. These values for the various elements were divided by those of Si to yield relative atomic ratios (Si = 1). The elemental sensitivity factors of O 1*s* = 1.00, Al 2*p* = 0.40, and Si 2*p* = 0.51 used in this work were obtained experimentally from samples of Al_2O_3 and SiO_2. The factor of Cl 2*p* = 1.95 was taken relative to Rh $3d_{5/2}$ = 4.20 to yield a stoichiometric Cl/Rh ratio for $RhCl_3 \cdot 3H_2O$. These factors should be compared with the calculated values (as described below) which were, respectively, 1.00, 0.38, 0.55, and 1.35. For the other elements calculated values were used. These were Na 1*s* = 0.60, C 1*s* = 0.52, Rh $3d_{5/2}$ = 4.20, and I $3d_{5/2}$ = 5.65, all of which were obtained with electron mean free paths in the zeolite except the Rh value which was obtained from a sample of $RhCl_3 \cdot 3H_2O$.

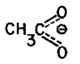
RESULTS

Infrared Studies

A summary of the key spectral features obtained are given in Table 1. Some of the

TABLE 1

Infrared Bands Observed on RhX

Treatment	Position of bands (cm^{-1})	Proposed surface species or additional species present	Ref.
(i) RhX vacuum (473 K, 16 hr)	1640 (br)[a] 1430 (w) 1485 (w)	Residual CO_3^{2-}; H_2O and $-OH^2$	(7)
(ii) RhX vacuum (473 K, 16 hr) CO (373 K, 1 hr, 13.3 kPa) vacuum (333 K, 5 min)	2025 (s), 2095 (s) 1640 (br) 1430 (w), 1485 (w)	$-Rh(CO)_2$	(7)
(iii) RhX vacuum (473 K, 16 hr) CO + CH_3I (373 K, 1 hr, 13.3, 13.3 kPa) vacuum (333 K, 5 min)	2085 (m) 1710 (vs) 1640 (br)	CH_3 | C=O | $-Rh(CO)$	(7)
(iv) Following (iii): vacuum (373 K, 1 hr)	1710 (sh) 1640 (br) 1585 (vs), 1470 (sh) 1435 (vs), 1380 (sh) 1330 (m)	 $CH_3C(\ominus)O_2$ + CH_3COOH (possibly CH_3COO^-–Rh)	This work

[a] br = broad, w = weak; s = strong; m = medium, vs = very strong, sh = shoulder.

spectra are given in Fig. 1. The bands due to formation of the acetylrhodium complex (7) are stable to evacuation at beam temperature (about 333 K), but the spectrum is greatly altered under evacuation for extended periods at 373 K (compare spectra A and B). A complete removal of the band at 2085 cm^{-1} occurs even though in the original dicarbonyl unit little loss in intensity occurred under similar conditions. Additionally there is an almost total loss of the band at 1710 cm^{-1} and the appearance of new bands at 1585, 1435, and 1330 cm^{-1}. Other bands originally present between 1370 and 1485 cm^{-1} are either reduced in intensity or, more probably, obscured by the new absorption peaks. Following this treatment the catalyst was reexposed to CO. A single band was produced at 2095 cm^{-1} and was unchanged in position and intensity by subsequent evacuation at 373 K for 1 h (spectrum C).

Spectrum D results from exposure of RhX or NaX after vacuum treatment at 473 K to acetic acid at beam temperature.

On exposing RhX to CO after the catalyst had been treated with acetic acid two absorptions were seen at 2095 and 2020 cm^{-1} and the spectrum E resembled that obtained following treatment of fresh RhX with CO alone.

None of the spectral features produced as described above with RhX or detailed in Table 1 were seen when using NaX, except for those due to residual CO_3^{2-}, H_2O, and -OH.

If RhX was exposed to a mixture of propyl-2-iodide and CO instead of CH_3I and CO, the spectrum obtained resembled that obtained with CO alone. There were no new bands below 2000 cm^{-1}.

When silica-supported rhodium trichloride underwent treatment with CO alone, bands were seen at 2040 and 2100 cm^{-1} with a relative intensity very close to that found for RhX (I_{2100}/I_{2040} about 1.5). Following treatment with CO and CH_3I the relative intensity of the band at 2040 cm^{-1} was lower, giving an intensity ratio of about 2.5). This limited loss was in contrast to the total loss of the low frequency band seen with RhX, and, in addition, there was no indication of the formation of an acylrhodium complex for the silica-supported sample.

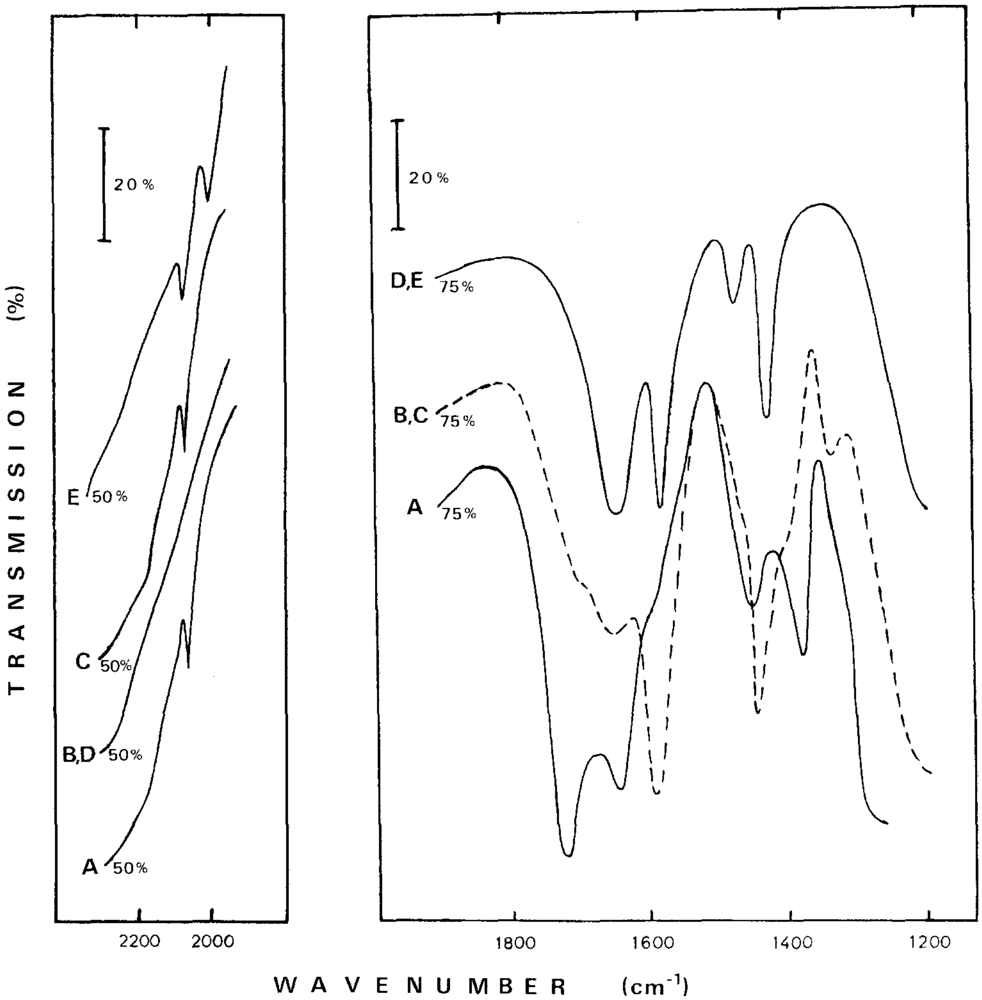


FIG. 1. Infrared spectra obtained for 13.3, adsorption on RhX. (A) RhX vacuum (473 K, 18 hr) followed by CO + CH_3I (373 K, 1 hr, 13.3, 13.3 kPa), then vacuum (333 K, 5 min). (B) After (A) followed by vacuum (373 K, 1 hr). (C) After (B) followed by CO (373 K, 1 hr, 13.3 kPa), then vacuum (333 K, 5 min). (D) RhX vacuum (473 K, 18 hr) followed by CH_3COOH (333 K, 5 min, 1.33 kPa), then vacuum (333 K, 5 min). (E) After (D) followed by CO (373 K, 1 hr, 13.3 kPa), then vacuum (333 K, 5 min).

ESCA Studies

In Table 2 binding energies and FWHM in electron volts are given for core lines from Rh-zeolites treated in various ways and from some reference compounds. The rhodium compounds were observed to be sensitive to the X-ray radiation. Several preparations of these samples were carried out. In addition, cooling of the sample was attempted. The color of the rhodium chloride and $HRh(CO)(PPh_3)_3$ was changed during the analysis, but no changes in the spectral features were noticeable. The RhX samples, especially those treated with CO and CH_3I, were, however, after several hours of X-ray exposure partly decomposed to some lower valence state for rhodium. Effort was taken, however, to ensure that spectra were obtained rapidly before any changes in the features were observable.

TABLE 2

Binding Energies and FWHM of Core Levels from Rh-Zeolite Catalysts and Some Reference Compounds

Compound	Rh $3d_{5/2}$	$\Delta 3d_{5/2-3/2}$	C $1s$	O $1s$	Na $1s$	Al $2p$	Si $2p$	Cl $2p$	I $3d_{5/2}$
$RhCl_3 \cdot 3H_2O$	310.2 (1.9)[a]	4.7		533.2 (3.1)				198.8 (3.1)	
$HRh(CO)(PPh_3)_3$	309.5 (3.2)	4.6	—[b]	532.0 (3.3)					
Al_2O_3				530.7 (2.5)		73.9 (2.2)			
SiO_2				533.0 (2.4)			103.9 (2.6)		
NaX (Same result with pretreatment at 473 K, 18 hr vac.)				531.7 (2.4)	1072.5 (2.2)	74.4 (2.2)	102.3 (3.0)	—	
RhX	310.2 (3.0)	4.7		531.7 (2.8)	1072.8 (2.3)	74.4 (2.6)	102.3 (3.5)	198.9 (3.9)	
RhX vacuum (473 K, 18 hr)	310.2 (2.4)	4.7		531.6 (2.7)	1072.5 (2.4)	74.4 (2.7)	102.3 (3.5)	198.5 (4.2)	
RhX O_2 (473 K, 18 hr, 0.1 MPa)	310.1 (2.2)	4.8		531.6 (2.7)					

TABLE 2—*Continued*

Compound	Rh $3d_{5/2}$	$\Delta 3d_{5/2-3/2}$	C 1*s*	O 1*s*	Na 1*s*	Al 2*p*	Si 2*p*	Cl 2*p*	I $3d_{5/2}$
RhX H_2 (603 K, 20 hr, 0.1 MPa)	307.8 (3.0)	4.6		531.5 (3.0)	1072.6 (2.6)	74.6 (2.6)	102.3 (3.9)	198.9 (4.3)	
Same treatment followed by: O_2 (298 K, 70 hr, 0.1 MPa)	308.6 (3.4)	4.6		531.7 (2.9)	1072.3 (2.8)	74.3 (2.9)	102.0 (3.9)		
RhX vacuum (473 K, 18 hr) CO (433 K, 1 hr, ~20 kPa)	310.1 (2.3)	4.7	~289	531.6 (2.6)	1072.3 (2.2)	74.3 (2.4)	102.2 (3.0)		
RhX vacuum (473 K, 18 hr) CO + CH_3I (433 K, 1 hr ~20. ~20 kPa)	310.0 (3.1)	4.6	~289, ~287	531.6 (2.7)	1072.4 (2.2)	74.5 (2.7)	102.6 (3.0)		619.0 (3.1)
Rh	307.1[c], 307.0[d]	4.7							
$RhCl_3 \cdot 3H_2O$	309.7[c], 310.3[d]	4.7		532.9[d]				199.5[c], 199.4[d]	
Rh_2O_3	309.1[d]			530.5[d]					

[a] FWHM in parentheses.

[b] C 1*s* from CO covered by C 1*s* from Ph group with satellite.

[c] Ref. (*40*).

[d] Ref. (*41*).

TABLE 3

Elemental Compositions of Zeolites Treated in Various Ways, Determined from ESCA Spectra (Ratios to Si)

Compound	Na	Al	Si	O	Rh	Cl	I	C(CO)	$C(CH_3)$
NaX	0.33	0.42	1	1.9	—	—			
NaX vacuum (473 K, 18 hr)	0.23	0.41	1	1.8	—	—			
RhX	0.18	0.46	1	1.8	0.047	0.0087			
RhX vacuum (473 K, 18 hr)	0.31	0.48	1	1.9	0.050	0.0082			
RhX H_2 (603 K, 20 hr, 0.1 MPa)	0.18	0.43	1	1.7	0.036				
Same treatment followed by: O_2 (298 K, 70 hr, 0.1 MPa)	0.18	0.47	1	1.9	0.040				
RhX vacuum (473 K, 18 hr) CO (433 K, 1 hr, ~20 kPa)	0.23	0.49	1	1.9	0.043			0.13	
RhX vacuum (473 K, 18 hr) CO + CH_3I(433 K, 1 hr, ~20, ~20 kPa)	0.17	0.59	1	2.1	0.052		0.015	0.062	0.14
Chemical composition of NaX	0.8	0.8	1.0	3.6[a]					
Chemical composition of RhX	0.8	0.8	1.0	3.6[a]	0.01				

[a] With water of hydration excluded.

Moreover, many preparations were made and the core lines were measured in different orders.

Comparisons with results from other workers on rhodium chloride are also given in Table 2. Their values are not in exact agreement with those obtained here and the discrepancies may be explained on the basis of differences in analyzer characteristics. The same reference level, namely, the C 1*s* line at 285.0 eV from carbon contamination, has been used.

Results from the quantitative estimations are given in Table 3. These calculations were performed according to the model of Carter *et al.* (*11*). The atomic ratio for two elements is given as

$$\frac{n_1}{n_2} = \frac{I_1}{I_2} \cdot \frac{\sigma_2 \lambda_2 S_2}{\sigma_1 \lambda_1 S_1},$$

where I_x is the intensity of one photoelectron signal from element x, σ_x the cross section for photoemission from that level, and S_x the transmission factor of the analyzer at the electron kinetic energy of the same signal. The elemental sensitivity factor $\sigma_x \cdot \lambda_x \cdot S_x$ has been both calculated and determined experimentally for some of the elements. The cross sections σ_x were taken from Scofield (*12*). The transmission function has been given by Barbaray *et al.* (*13*). The electron mean free paths were calculated for the various signals and compounds according to the procedure described by Penn (*14*). The correspondence between these sensitivity factors and those obtained experimentally for the elements in Al_2O_3 and SiO_2 is encouraging (see Experimental). The same comparison for $RhCl_3 \cdot 3H_2O$ is not as good. The absolute determination of the atomic ratios O/Si and Al/Si is thought to be better than 10%, while the error in those of Rh, Cl, C, Na, and I relative to Si is not known and may be as much as 50%. However, when comparing results for the same compound exposed to various treatments or present at different surface concentrations, etc., these differences can be more accurately determined. The maximum error in these relative determinations is then thought to be well below 10%, which is the highest deviation observed between two runs. The change in the amount of carbon contamination on the surface layer of the sample during a prolonged ESCA experiment led at worst to a 25% increase in the C 1*s* signal intensity. The core lines, at different kinetic energies, have different escape depths and their intensities are then reduced by different amounts. This effect is thought to provide the largest contribution to the maximum error in the relative determination. Throughout this work care was taken that all samples were oriented with the same angle in order to minimize discrepancies from this source.

Figure 2 shows Rh 3d electron spectra from rhodium chloride and from catalysts treated in various ways. These spectra are remarkably alike for rhodium chloride, RhX untreated, and RhX heated *in vacuo* or oxygen (spectra A, B, C, and E). If, however, the sample was exposed to prolonged heating under vacuum, a clear change in the peak shape was observed as shown in spectrum D. When simultaneously illuminated with the X-ray radiation this change occurred more rapidly, and furthermore there was also an increase in the relative intensity at an even lower binding energy than observed after vacuum treatment alone, compatible with a partial formation of metallic rhodium. RhX reduced with hydrogen yielded peaks differing from those obtained by vacuum decomposition (spectrum F). Spectrum G shows that the reduced sample could be reoxidized.

Figure 3 shows the effect on the Rh 3*d* electron spectra from RhX of treatment with CO alone and with a mixture of CO and CH_3I. CO adsorption (spectrum B) leads to no significant change in the original spectrum (spectrum A). The CO plus CH_3I adsorption (spectrum C) does, however, yield a significantly altered peak shape. This spectrum could be fitted with two pairs of Gaussian peaks. As with the other samples this specimen also showed a change in peak shape after prolonged illumination with X-rays. These new peak shapes could not, however, be fitted with only the two pairs of peaks shown in spectrum C, but needed an additional pair of Gaussian peaks at a lower binding energy.

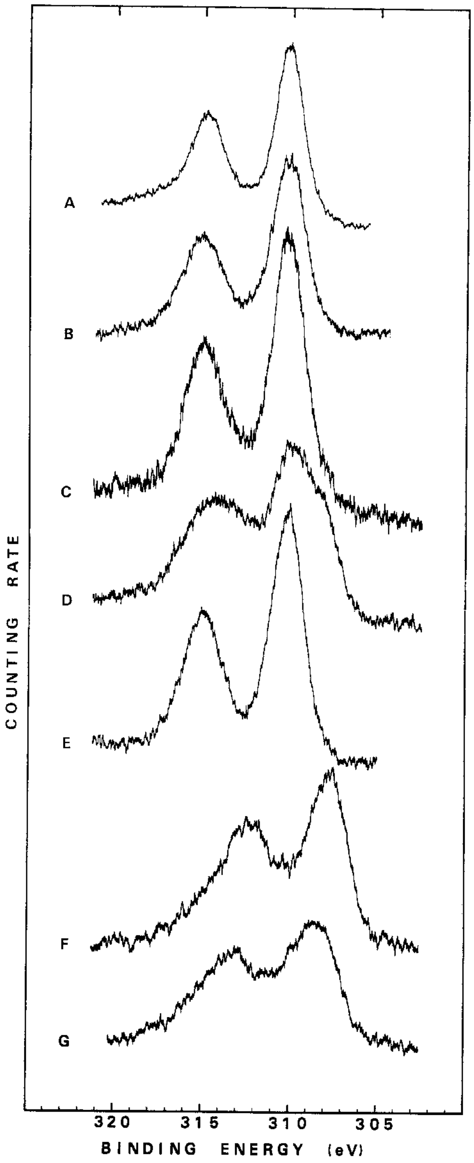


FIG. 2. Rh 3*d* electron spectra from $RhCl_3 \cdot 3H_2O$ and RhX treated in various ways. (A) $RhCl_3 \cdot 3H_2O$, (B) RhX, (C) RhX vacuum (473 K, 18 hr), (D) RhX vacuum (473 K, 90 hr), (E) RhX O_2 (473 K, 20 hr, 0.1 MPa), (F) RhX H_2 (603 K, 20 hr, 0.1 MPa), (G) after (F) followed by O_2 (298 K, 70 hr, 0.1 MPa).

Figure 4 shows the C 1*s* electron spectra from RhX after pretreatment *in vacuo* (spectrum A), after CO adsorption (spec-

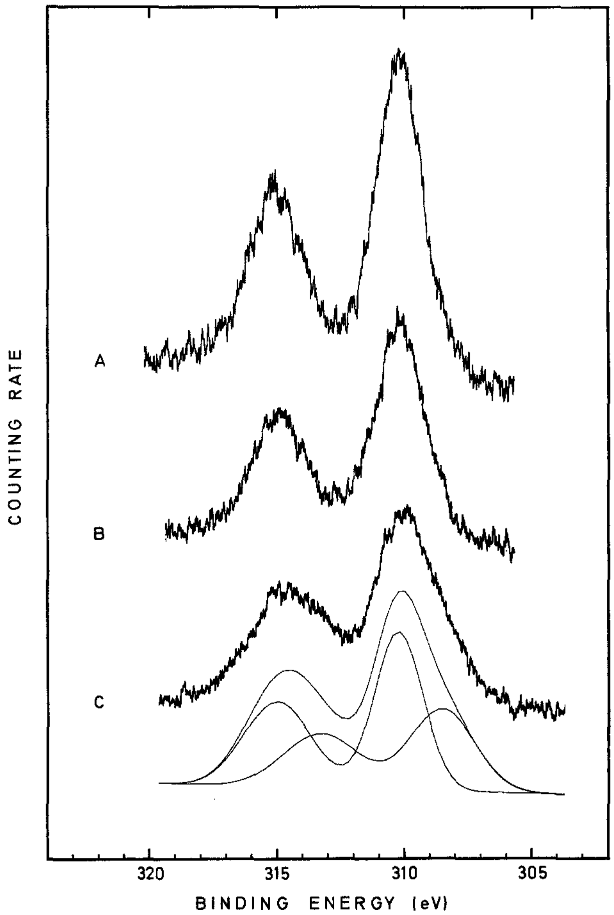


FIG. 3. Rh 3*d* electron spectra obtained from adsorption of CO and CO + CH_3I on RhX. (A) RhX vacuum (473 K, 18 hr). (B) RhX vacuum (473 K, 18 hr) followed by CO (433 K, 1 hr, ~20 kPa). (C) RhX vacuum (473 K, 18 hr) followed by CO + CH_3I (433 K, 1 hr, ~20, ~20 kPa).

trum B), and after CO plus CH_3I adsorption (spectrum C). Spectra B and C could be fitted with two and three Gaussian-shaped peaks, respectively. However, it is evident in spectrum B that the peak shape is somewhat more Lorentzian-shaped than pure Gaussian. The peak at low binding energy in spectra B and C is identical to that in spectrum A and is due to the carbon contamination (the small rise in background at higher binding energy in spectrum A may be due to trace CO_3^{2-} species present in RhX as revealed by the ir studies). The other two peaks at higher binding energy are due to the adsorbed species. The peak shapes in spectra B and C were not identically reproducible because of the varying amount of carbon contamination between different preparations. In fact, during prolonged ESCA runs, the carbon contamination peak increased in intensity, but the peak shape could still be fitted with two and three Gaussian peaks, respectively.

DISCUSSION

Infrared Studies

As outlined elsewhere (7) the spectral changes occurring after exposure of RhX

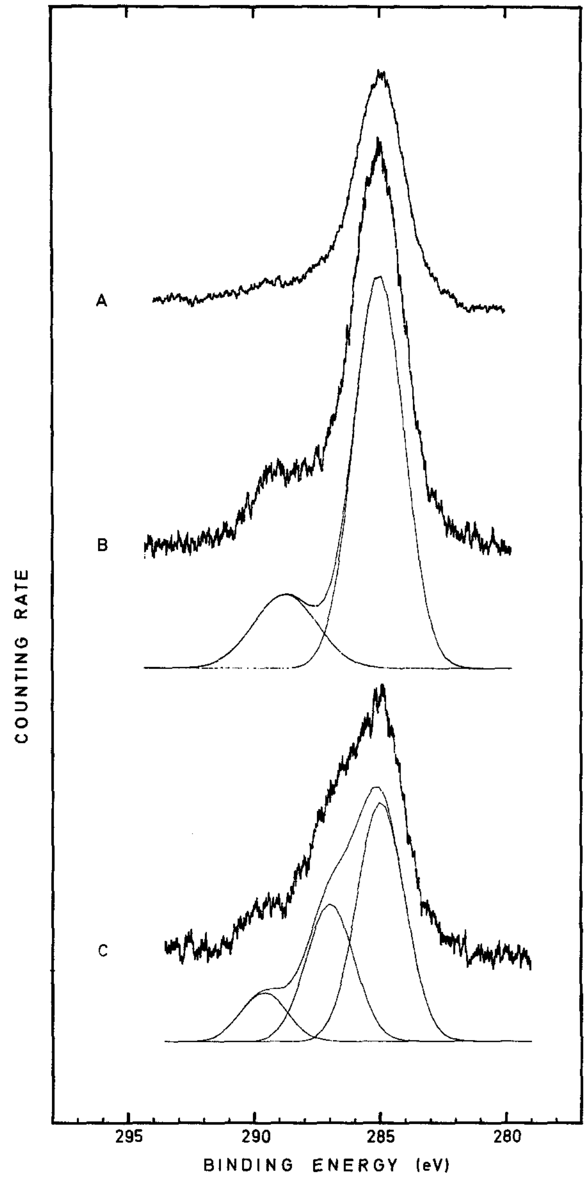


FIG. 4. C 1*s* electron spectra obtained from adsorption of CO and CO + CH_3I on RhX. (A) RhX vacuum (473 K, 18 hr). (B) RhX vacuum (473 K, 18 hr) followed by CO (433 K, 1 hr, ~20 kPa). (C) RhX vacuum (473 K, 18 hr) followed by CO + CH_3I (433 K, 1 hr, ~20, ~20 kPa).

to a mixture of carbon monoxide and methyl iodide at 373 K are readily interpreted as revealing the formation of an acetylrhodium species from reaction of the dicarbonylrhodium complex with methyl iodide. The dicarbonyl is itself produced by exposure of RhX to carbon monoxide alone at 373 K (*7*). These spectral and chemical features are in very close agreement with those found for rhodium in a homogeneous environment (*8*, *15*). Acylrhodium complexes are known to possess a characteristic carbonyl absorption at about 1700 cm^{-1} (*16–18*), and dicarbonylrhodium units usually exhibit two strong infrared bands between 2000 and 2200 cm^{-1} (*19–22*). It is felt that the rhodium in RhX is not in the metallic state. Although CO adsorbed on metallic rhodium does give rise to absorption bands above 2000 cm^{-1}, additional bands are always present below this position in the region 1800 to 1900 cm^{-1} (*23*, *24*). These low frequency absorptions were not seen in the present work.

The formation of rhodium carbonyls in zeolites has also been reported by others. Primet *et al.* (*25*) working with NaY ion-exchanged with $[Rh(NH_3)_5Cl]^{2+}$ observed formation of both $Rh^{I}(CO)_2$ and $Rh^{III}(CO)$ species, the latter being produced only at low levels of hydration. The two formal oxidation states may be distinguished on the basis of the positions of the infrared bands due to the carbonyl stretching vibrations, which lie at a higher wavenumbers for Rh(III). Following Primet *et al.* (*25*) and using spectral data reported by Forster (*22*) we conclude that the present ir results suggest formation of $Rh^{I}(CO)_2$ exclusively. A direct comparison of the two zeolite samples is made rather difficult, however, by the different method of preparation and pretreatment used. We have made no attempt to carry out incorporation of rhodium by classical ion-exchange with a well-defined cationic starting material because the resulting catalysts are only marginally more active per unit of rhodium in carbonylation (*2*). It seems that the rhodium dispersion in our case is not very high (see ir data and ESCA data, below) and it is probable that the rhodium is for the most part present on the external surface of the support. The importance of experimental procedure on the nature of the rhodium species produced is underlined by the results of Mantovani *et al.* (*26*) who suggest that carbonylrhodium clusters are formed by treatment of an ion-exchanged NaY zeolite with H_2/CO mixture at high pressure. Our own experimental procedures for recording both ir and ESCA spectra originate from the desire to treat samples in a manner which is as closely consistent as possible with the production of active carbonylation catalysts (*1–4*).

The profound changes in the spectrum seen on treating the catalyst at 373 K for extended periods after formation of the acetylrhodium complex had taken place result in a spectrum which is essentially identical to that obtained by exposing RhX (or NaX) to acetic acid vapor. Thus it is apparent that conversion of the acetyl complex is taking place due probably (*6*) to the hydrolytic action of water present in RhX. After such a relatively mild pretreatment at 473 K a considerable quantity of water remains in the catalyst—a very intense and broad absorption band is seen in the region 4000 to 2700 cm^{-1} such that it is not possible to use this part of the spectrum to obtain, for example, information about the carbon–hydrogen stretching vibrations of the various adsorbed species. The hydrolysis reaction produces acetate ions (bands at 1585 and 1435 cm^{-1} (*27*)), but some un-ionized acetic acid is also present (band at 1330 cm^{-1}; additional band expected near 1440 cm^{-1} (*27*) obscured). Since these bands are generated at the expense of the band at 1710 cm^{-1} the spectral features strongly support the contention ((*5–7*) that the acetyl complex functions as a vital intermediate in the catalytic carbonylation of methanol on this catalyst. The absence of a corresponding acyl formation with propyl-2-iodide is entirely consistent with the known difficulty of conducting carbonylation reactions of propyl-2-ol/propyl-2-iodide mixtures on RhX (*3*).

The observation that only one band at 2095 cm^{-1} appears on admission of carbon monoxide to RhX following conversion of the acetyl complex to acetic acid and acetate entities suggests that either the catalytic cycle does not involve a return to the dicarbonylrhodium complex, or that the cycle is not in fact completed under the conditions employed here. It is very unlikely that formation of the dicarbonyl unit is physically hindered by the presence of acetic acid and acetate ions on the surface because of the results depicted in Figs. 1D and E. These spectra show that the dicarbonyl state is realized when CO is adsorbed on RhX which has been exposed to acetic acid vapor but which has not previously been contacted with CO. The catalytic cycle could be incomplete in this work if the acetate ions produced from acetylrhodium are still coordinated to the rhodium center. Acetate ions formed by the direct adsorption of acetic acid on RhX are conceivably present on the zeolite support leaving the rhodium centers free.

Finally, it should be noted that the absence of formation of an acylrhodium species for silica-supported rhodium chloride, despite the fact that the dicarbonyl unit is produced in the same way as for RhX, may suggest that the dicarbonyl–acetyl conversion is strongly influenced by the nature of the carrier used. It seems probable that the nature of the surface rhodium is dependent on the type of support and that only RhX is suitable for acetyl formation as a consequence of a special promoting action of the zeolite. As noted above, however, the function of the zeolite in this context does not appear to be connected with the formation of rhodium units in a highly dispersed state within the supercages of the lattice. Nevertheless, that some structural influence is of importance is suggested by the observation (*2*) that amorphous silica–aluminas do not produce satisfactory carbonylation catalysts when they are used as the support. A deeper insight into the reasons for this must await the stage when a thorough comparative characterization of the rhodium species present on the various carriers has been achieved.

An estimate of the concentration of dicarbonylrhodium complex may be made by consideration of the intensities of the bands at 2025 and 2095 cm^{-1} seen on treating RhX with CO at 373 K. If N is the number of such complexes per gram of catalyst, then N is given by $I\,N_0\,S/\epsilon\,m$, where I is the integrated intensity of the bands, N_0 is Avogadro's number, ϵ is the integrated molar extinction coefficient, and m and S are the mass and geometric area of the catalyst sample, respectively. In this work $S/m = 40\ \text{cm}^2\ \text{g}^{-1}$. Computing I as $I = A\Delta\nu_{\frac{1}{2}}$, where A is the measured optical density of the bands and $\Delta\nu_{\frac{1}{2}}$ is the bandwidth at half peak height, then I is $\sim 22\ \text{cm}^{-1}$ for the two bands at 2025 and 2095 cm^{-1} when summed together. For ϵ a value of $6\cdot 10^8$ cm mol^{-1} is taken. This is the value measured here for a complex such as $HRh(CO)(PPh_3)_3$ in benzene and is also a typical value for transition metal carbonyls (*28*). N is then computed as $4.4\cdot 10^{17}$ dicarbonyl complexes g^{-1}. Since for RhX there are $3.6\cdot 10^{19}$ rhodium atoms g^{-1}, it is seen that the results are consistent with the involvement of only ca. 1% of the bulk rhodium in formation of surface carbonyl complexes. It seems probable that since ion-exchange has not been employed, for a rhodium content of ca. 0.6 wt% the dispersion is not particularly high, and this view is supported by the observation that the carbonlyation activity per unit weight rhodium in rhodium trichloride–NaX catalysts increases with decreasing rhodium content (*1*).

ESCA Studies

In Table 2 it can be seen that the O 1*s*, Al 2*p*, and Si 2*p* binding energies (B.E.) are somewhat different in the zeolite (NaX) than in the compounds Al_2O_3 and SiO_2. Thus the Al 2*p* B.E. has a higher value in NaX corresponding to the extra positive charge conferred on the aluminium atoms by the coordination of one extra oxygen atom in the zeolite structure as compared with the Al_2O_3. This also reflects the more acidic nature of Al in the zeolite. The Si 2*p* has a considerably lower value in the zeolite than in SiO_2. The Si atoms are more negatively charged in the zeolite, possibly arising from Si being more electronegative than Al. The O 1*s* B.E. in the zeolite is in between the value for Al_2O_3 and SiO_2 in accordance with the shifts for Al and Si. A possible objection is that the method of referring binding energies to carbon contaminations may induce some errors. However, since no internal standard is available and other methods of charge compensation are not considered superior to any substantial degree, this method has been chosen.

In Table 3 the elemental compositions are shown, which for the zeolite clearly deviates from the chemical composition. The Al/Si and O/Si ratios obtained from the ESCA spectra are about half of the expected values. This indicates that the zeolite is enriched with Si (dealuminated) in the surface layer, which also has been reported for type A (*29*) and for type A, X, Y, and Z zeolites (*30*). It seems clear that care should be taken when comparing literature data from various sources, since all effects concerning quantitative ESCA analysis may not have been considered thus leading to discrepancies which may be the result of the use of inaccurate elemental sensitivity factors. The calculation of the sensitivity factors (described above) for O 1*s*, Al 2*p*, and Si 2*p* yielded the same values in Al_2O_3 and SiO_2 as in NaX. Thus this discrepancy is not considered as arising from a matrix effect. The values for the Na content are less than one-half of that expected. Results contrary to these have also been reported (*25*, *31*, *32*), but here, in general, only theoretical cross sections without any corrections have been used. Furthermore these reports do not concern the same zeolite and source of manufacture. The sodium content of the various samples in Table 3 fluctuates somewhat which may arise as the result of a heterogeneous sodium distribution. Using ESCA, Stork *et al.* (*29*) have obtained similar results for type A zeolites although only after ion-exchange and comparable observations are reported by Finster *et al.* (*31*). The effect of heating NaX *in vacuo* at 473 K for 18 hr is that water is removed. There are no significant changes in the ESCA spectra.

With the rhodium ion-exchanged zeolite (RhX) there were no changes in Al 2*p*, Si 2*p*, or O 1*s* signals, but a slight broadening of all peaks which might arise from a differential sample charging effect could be detected (see Table 2). As a new feature Rh and Cl signals have appeared. The Rh $3d_{5/2}$ and Cl 2*p* peaks have the same B.E. as those of the rhodium chloride, but are broadened (Fig. 2 and Table 2). The quantitative estimations (Table 3) show that, based on the observed Cl content of RhX, less than 5% of the rhodium atoms are in the form of $RhCl_3 \cdot 3H_2O$. (The Cl 2*p* sensitivity factor has been taken to fit $RhCl_3 \cdot 3H_2O$.) The chlorine detected need, however, not be in this form and it is uncertain if any $RhCl_3$ exists at all in the surface layer. It is evident that the rhodium atoms have the same valency state in RhX as in the chloride. The Rh/Si ratio is around 0.05, considerably higher than the expected 0.01, which probably reflects the existence of an ion diffusion gradient within the zeolite particles during catalyst preparation. Considerably higher values than expected have also been reported for Cu, Co, and Fe ion-exchanged type A zeolites (*29*).

The effect of heating *in vacuo* at 473 K for 18 hr is that water is removed and for NaX no significant changes in the spectra occur. With RhX, however, there is a slight narrowing of the Rh $3d_{5/2}$ signal (see Table 2 or Fig. 2), possibly indicating that the water molecules coordinated to the Rh atoms have desorbed and that the environment of all surface Rh atoms has become more uniform. This is particularly interesting, considering that only catalysts treated this way are active (*3*). The heat treatment in oxygen gave similar results. A prolonged heat treatment *in vacuo* produces a Rh $3d_{5/2}$ spectrum as shown in Fig. 2D. It is evident that some part of the Rh atoms has been reduced to a lower valence state, and possibly several valence states coexist, including the metallic state. It seems reasonable that even the samples treated for 18 hr may contain a very small percentage of the reduced form of Rh. However, it is a too small part to be detected in the spectra.

To investigate the stability toward reduction in hydrogen, treatment at atmospheric pressure for 20 hr at 603 K was performed. It can be seen in Fig. 2 and Table 2 that a major part of the Rh species has been reduced to the metallic state. The origin of the changes in the Rh/Si ratio shown in Table 3 is not known. Possibly it indicates that during the reduction the Rh atoms have agglomerated into small metal particles. When treating this sample with oxygen the Rh metal is reoxidized, possibly to Rh_2O_3, as seen in Fig. 2G and Table 2. This reduction–reoxidation behavior has been described for several ion-exchanged type Y zeolites, although quantitatively the effect is somewhat different for other metals (*33*).

When adsorbing CO on the pretreated catalyst, the only essential change is displayed by the C 1*s* signal (Tables 2 and 3 and Fig. 3). That carbon monoxide has been adsorbed is shown by the left signal at higher B.E. in Fig. 4B. The left signal has an unexpectedly high B.E. compared with values for CO adsorbed on tungsten (*34*), where the highest B.E. observed was ~287 eV due to linear adsorption via the carbon atom. Adsorption on (or rather coordination to) Rh in an oxidized form is undoubtedly not comparable with that on metallic tungsten. This is evident considering the shift of +3 eV in the position of the C 1*s* signal from the CO ligands relative to the CH_3 group in $CH_3COMn(CO)_5$ (*35*), or a value of 289.1 eV for the carbonyl ligands in $Cr(CO)_6$ (*36*). The fact that no significant changes in the Rh signal could be detected when CO adsorption took place can be explained by back donation from some rhodium orbitals to the CO molecule, with an increase in electron density at the oxygen atom. It should be possible to tell this from the O 1*s* signal, but the intensity of this signal (calculated from the C 1*s* signal of CO) is very much lower than the O 1*s* signal from the zeolite, which totally covers it. No detectable changes in the O 1*s* spectra due to CO are then to be expected. It should be remarked that for a preparation obtained by ion exchange of NaY with $[Rh(NH_3)_5Cl]^{2+}$ a change in the Rh line was observed after interaction with CO at atmospheric pressure for 4 hr, following pretreatment of the sample at high temperature (500°C) in oxygen (*25*). Such a contrasting result may well arise as a result of the significantly different procedures adopted in the preparation and treatment of the sample.

It may be deduced from Table 3 that approximately three CO molecules per rhodium atom are adsorbed. This figure is felt to be uncertain because no calibration of the cross sections for Rh $3d_{5/2}$ relative to C 1*s* could be made for reasons of there being no suitably accessible stable reference compound. A carbonyltriphenylphosphine complex was tried (see Table 2), but the phenyl carbon signal completely dominates the spectra and it is not possible to attribute any feature of this C 1*s* spectrum to the CO carbon.

The adsorption of both CO and CH_3I yields, as was the case with pure CO, no effect on the support material signals (see Table 2). The Rh $3d_{5/2}$ signal, however, has broadened asymmetrically toward lower binding energy. In Fig. 3 it is shown that this Rh 3*d* spectrum can be fitted with two pairs of Gaussian peaks, with the new $3d_{5/2}$ peak at ~308.5 eV. A substantial change in charge on these rhodium species as a result of the interaction with CO and/or CH_3I is thus detected. It is uncertain whether this should be described as a change in formal valence state of the rhodium ions, or simply as a change in ligands resulting in an alteration in the charge distribution. Shifts with more than 2 eV between various Rh(III) complexes with different ligands have been reported (*37*).

The other new features in the ESCA spectra after CO and CH_3I adsorption are, as is shown in Table 2, two new C 1*s* signals and one I $3d_{\frac{5}{2}}$ signal. The C 1*s* spectrum is shown in Fig. 4C. This spectrum could be fitted with three Gaussian peaks, and the two at higher B.E. are referred to as CO and CH_3, respectively. The amounts are shown in Table 3 to be 0.06 and 0.14, respectively. The variation was about 50% between different preparations, although the CH_3 signal always seemed to be the greater one. When comparing their intensity to the Rh intensity, one CO and two or three CH_3 groups should be coordinated to each Rh ion. These figures are, however, as in the CO adsorption case, highly uncertain. In the CO adsorption case approximately three coordinated groups per Rh species were detected, and in the CO plus CH_3I case there were also approximately three such groups, regarding the major part of the CO to be present in the acyl form. Thus it seems likely that the rhodium ions in the zeolite have three ligand positions available for coordination of the reacting molecules.

The C 1*s* signals at ~289 and ~287 eV are thought to be due to CO and CH_3 groups, respectively. When comparing with Fig. 4B, it can be seen that the C 1*s* from the CO group has a higher B.E. when coadsorbed with CH_3I than for pure CO adsorption. This points to some interaction between these two groups, and it seems highly possible that an acetyl group has been formed. Calculations for some metal–acyl complexes show that a greater positive charge is to be expected on the keto carbon than on the carbonyl carbon (*38*), consistent with the conclusions drawn here. It is, however, confusing that data for $(CH_3CO)Mn(CO)_5$ (*35*) have been interpreted on the basis of a somewhat lower binding energy for the keto carbon than for the carbonyl carbon.

The iodine $3d_{\frac{5}{2}}$ B.E. is consistent with the value reported for a Rh complex (*37*). It can be seen in Table 3 that the iodine amount is only about one-tenth of the CH_3 carbon. As has been stressed in the other cases above, the elemental sensitivity factors used may be in error. A factor of 10, however, seems to be too great a fault to be realistic, and the iodine content is evidently much smaller than the CH_3 amount detected. Also it is lower than the Rh content, and this points to the fact that the methyl iodide is adsorbed dissociatively, and during this process (or afterward) "I" may leave the Rh- species in some form. This might very well be due to some solvolytic decomposition of the acetyliodorhodium complex which is considered (*5*, *6*) as a step in the overall mechanism of acetic acid production: e.g.,

$$(CH_3CO)RhI + H_2O \rightarrow CH_3COOH + HI + Rh.$$

Since that part of the Rh $3d_{\frac{5}{2}}$ signal which has been shifted represents an Rh amount of the same magnitude as the iodine content, it seems likely that the shift is caused by the iodine coordination. It is consistent with the partial shift parameter for I in Rh compounds which is −0.3 (*39*).

CONCLUSIONS

Several aspects of the ir and ESCA investigations are in very good agreement and are consistent with the catalytic behavior of RhX in methanol carbonylation. Both techniques reveal the presence of multicarbonyl rhodium species formed by adsorption of CO alone and the production of an acetyl complex if CO and CH_3I are coadsorbed. The ir data alone suggest that the rhodium carbonyl contains Rh(I) and not Rh(III) and furthermore only about 1% of the *total* rhodium in RhX is involved in the adsorption of CO. However, in the ESCA work the CO/Rh ratio is ~1, and a very high degree of involvement of *surface* rhodium with CO is therefore indicated. In addition, the ESCA data support the idea that it is rhodium in an oxidized form which participates in these surface reactions and which is therefore probably responsible for the carbonylation activity (*2*). Any definite statements regarding formal oxidation states from ESCA data alone may be rather dubious and are not offered. A significant feature of the catalyst composition revealed by ESCA is that the rhodium present in RhX is not, at least at the surface, in the form of rhodium trichloride. The exact chemistry of the evolution of the rhodium state at the surface on RhX is not clear at this stage, but the zeolite lattice may have a special ability to react with rhodium trichloride to produce rhodium in a bound, oxidized, and reactive state.

It is recognized that some doubts concerning the quantitative interpretation of some ESCA data are to some extent justified until further experiments with more elaborate calibration standards are devised and carried out, since the procedure for calculating the elemental sensitivity factors has not yet proved to be completely reliable.

ACKNOWLEDGMENT

One of us (S.L.T.A.) is grateful to Professor S. T. Lundin for his generous support during the course of this work.

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