Studies by ESCA of Supported Rhodium Catalysts Related to Activity for Methanol Carbonylation

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Various solid preparations containing rhodium have been examined using ESCA in an attempt to provide a basis for understanding their activities in carbonylation of methanol to acetic acid. High activity is apparently associated with the use of molecular sieve zeolites as supports. With use of the pentammine rhodium salt [Rh(NH$_3$)$_5$Cl]Cl$_2$ the dispersion of rhodium in the zeolite framework is superior to that found using RhCl$_3$ All active preparations contain rhodium predominantly in the +3 state. The realization of this oxidation state in the initial catalyst may be a necessary but insufficient requirement for subsequent activity for carbonylation. RhCl$_3$/MgO also contains Rh(III) but no catalyst activity is seen. For RhCl$_3$/SiO$_2$ and RhCl$_3$/SnO$_2$, there is a clear tendency for Rh(I) species to be produced in the initial material and these supports also lead to inactive catalysts. There is evidence that the zeolite framework assists in producing active sites by enabling the ligands originally surrounding the rhodium centre to be easily removed so that coordination with the reactants present under reaction conditions can proceed with comparative ease. A further positive effect of the zeolite lattice operating under carbonylation reaction conditions in assisting the dissociative adsorption of methyl iodide is also suggested.

INTRODUCTION

Supported rhodium catalysts active in the gas-phase carbonylation of methanol have recently gained considerable attention (1–5). The activity of these preparations based on the use of oxide carriers, including molecular sieve zeolites, is very dependent on the nature of the support chosen. Thus magnesium oxide and zinc oxide confer no detectable activity, whereas zeolites (type 13X) enable rates to be obtained which in certain cases (3, 4) are comparable with those found using homogeneous catalysts (6). For silica-supported Rh cata-

lysts conflicting results have been reported (3, 5).

The most active zeolite catalysts appear to be those produced by ion exchange using, for example, solutions of the pentammine complex [Rh(NH$_3$)$_5$Cl]Cl$_2$ (3). In earlier studies (7) rhodium trichloride was used instead but the resulting catalysts are lower in specific activity by factors of about 50–100 (3). These less active preparations have been examined using a combination of infrared spectroscopic and ESCA techniques and the essential features of the surface chemistry thereby revealed (8).

It is still unclear, however, why the use of a zeolite support enables superior carbonylation activities to be achieved and in addition why Rh(NH$_3$)$_5$ClX is more active compared with RhCl$_3$X. In order to exam-

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ine this aspect we now report results of a study by ESCA which, although dealing chiefly with the $Rh(NH_3)_5ClX$ catalyst, also covers some of the other less active supported preparations. Some comparison is possible with parallel infrared spectroscopic examinations which clearly indicate that the adsorptive and surface chemical properties of rhodium are greatly influenced by the nature of the carrier selected (3, 8, 9).

This work is partly concerned with RhX zeolites, but interesting conclusions may be drawn in comparison with previous studies on RhY zeolites including those of Primet et al. (10, 11) and of Okamoto et al. (12).

EXPERIMENTAL

The catalysts examined were samples identical to those used earlier for methanol carbonylation (3, 7) and other spectroscopic studies (3, 8, 9). The series consisted of $RhCl_3X$, $Rh(NH_3)_5ClX$, $RhCl_3/SiO_2$, $RhCl_3/MgO$, $RhCl_3/SnO_2$ and $Rh(NH_3)_5Cl/mordenite$. Tin(IV) oxide was a gift from the Tin Research Institute, Middlesex, England, and the mordenite was Zeolon 900Na obtained from Norton Chemical Process Products Ltd. The other supports have been described elsewhere (3, 7).

The zeolites were exposed to aqueous solutions of the pentammine rhodium salt at 40–50°C for a few hours. Filtration yielded the solid which was dried overnight at 60°C. All other catalysts were prepared by impregnation of the support with an aqueous solution of rhodium trichloride (incipient wetness technique under ambient conditions) followed by drying of the material at 60°C. All preparations had a nominal rhodium content of 0.6 wt%, which in the case of the X-zeolites corresponds to an average of 1.0 Rh per unit cell. For mordenite as carrier the figure is 0.2 Rh per unit cell.

Measurements were performed with an AEI ES200B electron spectrometer which has been described in detail elsewhere (8). For the $RhCl_3/MgO$ catalyst, however, $MgK\alpha_{1,2}$-radiation was used to eliminate

interference with Mg KLL Auger Lines. Sample colours during various treatments were observed through a lead window. Procedures adopted for pretreatment of samples and for quantitative analysis of spectral data are as used previously (8). However, in this work N $1s$ and Cl $2p$ sensitivity factors have been determined using $[Rh(NH_3)_5Cl]Cl_2$ which give values of 0.65 and 1.3, respectively. For samples originating from $RhCl_3$ a Cl $2p$ sensitivity factor of 1.95 was used (8).

The original construction of the spectrometer with very small dimensions in the X-ray gun leads to a substantial heating of the sample. In order to reduce this effect the instrument was modified and equipped with an extra water cooler fitted onto the X-ray cap, an approach originally suggested for minimizing levels of hydrocarbon contamination (13). With such extra cooling no detectable heating of the sample occurs whereas it might otherwise be as large as about 80°C. Rh $3d$ spectra were usually obtained within the first 10–15 min of exposure of the samples to the X-ray beam in order to reduce radiation-induced decomposition.

In this work charging effects have been corrected for by evaporating gold in appropriate amounts at a pressure of approximately 10^{-5} Torr (Jeol instrument JEE 4B) and placing the Au $4f_{7/2}$ line at 84.0 eV. Several preparations were also examined without incorporating gold and in these cases correction was carried out by checking that the constant core lines of the support (given in Table 2) coincided with the values obtained by calibration with gold.

Some spectra were digitized and smoothed (14) on a Tetronix 4051 linked to a 4662 interactive digital plotter. Where appropriate, simulation of peak envelopes was carried out by adjusting the selected Gaussian components until a correct fit with the original peak was obtained. When dealing with Rh $3d$ lines in this way the procedure is necessarily somewhat approximate due to the curvature of the baseline
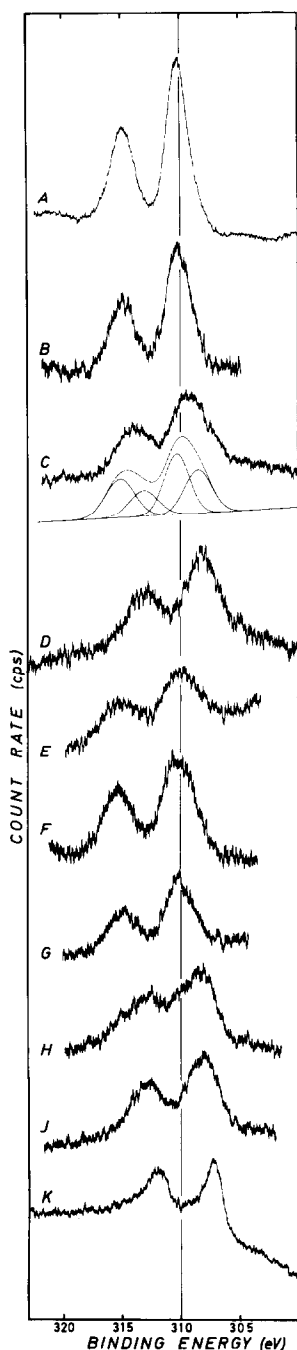
originating from the superimposed C $1s$ inelastically scattered peak.

RESULTS AND DISCUSSION

The binding energies (BE) and half-widths of some selected core levels for the Rh zeolites and relevant reference compounds together with some elemental compositions derived from the spectra are given in Table 1. Results for the other catalysts are included in Table 2 which also contains data on the spectra together with elemental compositions. Some of the original spectra are depicted in Fig. 1. Reference to valence states for Rh according to literature values for Rh $3d_{5/2}$ BE are included in Table 1.

Referring to the summarized elemental compositions of the various catalysts presented in Tables 1 and 2 the objection may be made in view of recently published material (15) that the use of the Si $2p$ peak as base is perhaps unreliable. This arises because there is the potential for interference from *Brehmsstrahlung*-induced Al KLL Auger peaks which can be of considerable intensity. Such doubts are not justified, however, since the relative magnitude of this effect has been examined in the present work by investigating the Si $2p$/Si $2s$ intensity ratios for silica and various zeolites. It is found that the intensity of the Si $2p$ lines in zeolites is enhanced by only about 4%.

The results are presented and discussed for: *Activation reactions* which includes examination of the original untreated catalysts, and catalysts after subjection to various pretreatments, some of which are typically used in activating catalysts for carbonylation, and *Carbonylation reactions* involving treatment of catalysts with carbon monoxide or mixtures of carbon monoxide and methyl iodide. Finally, the *Effect of the support* is described and discussed.

FIG. 1. Rh $3d$ electron spectra for some Rh-containing samples (for each spectrum, first temperature is that at which analysis was performed). (A) [Rh(NH₃)₅Cl]Cl₂, 10°C; [(B)–(J), Rh(NH₃)₅ClX]: (B) −80°C; (C) −80°C, after 1 h of analysis; (D) 400°C, vacuum (400°C, 0.5 h); (E) −60°C, vacuum (400°C, 0.5 h); (F) 25°C, O₂ or N₂ (400°C, 0.5 h, 1 atm); (G) 25°C, CO (100°C, 17 h, 1 atm) or CO + CH₃I (100°C, 15 h,

225 + 225 Torr) after O₂ (450°C, 4–5 h, 1 atm); (H) 25°C, CO + H₂O (svp at 25°C) (100°C, 20 h, 1 atm) after O₂ (450°C 2 h, 1 atm); (J) 25°C, H₂ (340°C, 1.5 h, 1 atm) after O₂ (400°C, 0.5 h, 1 atm); (K) Rh/C (5%), 25°C, vacuum (400°C, 2 h).

TABLE 1

Binding Energies and Half-widths of Core Levels and Elemental Compositions[a] from Rh Zeolite Catalysts and Some Reference Compounds, Together with Selected Literature Data

Compound	Treatment	Temp (°C) ESCA anal.	Rh/Si	Rh $3d_{5/2}$	Cl $2p$	N $1s$	Spectrum in figure
(Rh(NH₃)₅Cl)Cl₂		10		310.2 (2.0) 1.0	198.5 (3.1) 3.0	399.9 (2.1) 5.0	1A
Rh(NH₃)₅ClX		25, 10, −80 −100	0.017	310.2 (2.5) 1.0	198.7 (3.2) 1.0	400.0 (2.8) 5.3	1B
	Vacuum (400°C, 0.5 h)	200, 400	0.018	308.2 (3.2) 1.0	199.4 (3.2) 0.7	399.1 (3.5) 1.9	1D
	Vacuum (400°C, 0.5 h)	−60	0.018	309.9 (3.9) 1.0	199.1 (3.5) 1.1	400.2 (2.5) 4.2	1E
	N₂ or O₂ (400°C, 0.5 h, 1 atm)	25	0.017	310.2 (3.1) 1.0	199.2 (2.7) 1.8	400.2 (2.9) 2.4	1F
	O₂ (420°C, 23 h, 1 atm-flow)	25		310.2 (3.1) 1.0	199.4 (3.4) 1.0	400.4 (2.7) 2.0	
	H₂ (340°C, 1.5 h, 1 atm) after O₂ (400°C, 0.5 h, 1 atm)	25	0.011	308.2 (3.2) 1.0	199.1 (3.2) 2.0	399.9 (3.2) 2.1	1J

CO (100°C, 17 h, 1 atm) after O₂ (450°C, 4 h, 1 atm)[b]	25	0.016	310.2 (3.2) 1.0	199.7 (3.5) 1.2	400.3 (2.9) 2.3	1G
CO + CH₃I (100°C, 15 h, 225 + 225 torr) after O₂ (450°C, 5 h, 1 atm)[c]	25	0.014	310.2 (2.8) 1.0	"I 3d₅/₂" =	619.0 (2.6) 1.7	1G
CO + H₂O (svp at 25°C) (100°C, 20 h, 1 atm) after O₂ (450°C, 20 h, 1 atm)[d]	25		308.4 (4.1) 1.0	199.4 (3.5) 1.4	400.2 (2.9) 0.9	1H
N₂-flow (600°C, 5 min)	25		307.3 (2.9)			
Rh/C (5%) Vacuum (400°C, 2 h)	400		307.3 (2.2)			

Rh 3d₅/₂

Reference compounds	
Rh(I)	307.6–309.6 (Ref. (22))
Rh(II)	308.4–309.3 (Ref. (23))
Rh(III)	309.0–310.6 (Ref. (24))
Rh(III)	308.8–311.3 (Ref. (22))

[a] For each compound: First line is B.E. (eV), second line FWHM (eV, within parentheses) and third line atomic ratios calculated from the corresponding levels.
[b] White after O₂ or N₂, reddish brown after CO.
[c] White after O₂, light brown after CO + CH₃I.
[d] White after O₂, slightly fawn after CO + H₂O.

TABLE 2

Binding Energies and Half-widths of Core Levels and Elemental Compositions for some Rh-Containing Samples[a]

Compound	Temp (°C) ESCA anal	O 1s	Na 1s	Al 2p	Si 2p	Rh 3d$_{5/2}$	Cl 2p	N 1s
RhCl$_3$X[b]	-30	531.4	1072.0	74.4	102.4	310.2	199.3	
		(2.6)	(2.2)	(2.3)	(2.5)	(2.1)	(≅3)	
		3.5	0.86	0.65	1	0.075	0.008	
Rh(NH$_3$)$_5$ClX	25, 10, -80, -100	531.4	1072.1	74.4	102.5	310.2	198.7	400.0
		(2.5)	(2.2)	(2.4)	(2.5)	(2.5)	(3.2)	(2.8)
		3.2	0.79	0.60	1	0.017	0.017	0.090
						1	1	5.3
NaX[c]	-30	531.4	1072.1	74.5	102.5			
		(2.3)	(2.2)	(2.3)	(2.5)			
		3.0	0.84	0.60	1			
RhCl$_3$X (Theoretical composition)		3.6	0.66	0.8	1	0.010	0.03	
Rh(NH$_3$)$_5$ClX (Theoretical composition)		3.6	0.75	0.81	1	0.010	0.010	0.050
	-30	531.8	1071.8	74.3	102.7	310.2	198.8	400.1
		(2.7)	(2.3)	(2.5)	(2.5)	—	(3.6)	(2.4)
		2.4	0.16	0.19	1	0.013	0.013	0.047
		(Mg = 0.2)				1	1	3.6
Mordenite (Zeolon 900 Na)	-30	531.8	1071.7	74.2	102.8			
		(2.7)	(2.2)	(2.4)	(2.4)			
		2.3	0.13	0.16	1	(Mg = 0.2)		
Rh(NH$_3$)$_5$Cl/mordenite (Theoretical composition)		2.44	0.22	0.22	1	0.005	0.005	0.025
RhCl$_3$/SiO$_2$	-20	533.0			103.9	308.6	—	
		(2.7)			(2.7)	(3.4)		
		1.84			1	0.0012		
RhCl$_3$/MgO (Mg K$\alpha_{1,2}$-radiation)	25	531.2			*Mg 2s* 88.6	309.8	198.9	
		(2.3)			(2.6)	(3.5)	(3.3)	
		1.17			1	0.0067	0.0087	
						1	1.3	
RhCl$_3$/SnO$_2$	-10	529.7			*Sn 3d$_{5/2}$* 485.5	308.2	197.9	
		(3.2)			(2.5)	(3.1)	(3.4)	
		2.93			1	0.011	0.033	
						1	3	
RhCl$_3$/SnO$_2$ (Air 600°C, 2 min, until colour change)	-10	529.7			485.7	308.3	198.4	
		(2.2)			(2.2)	(2.4)	(3.4)	
		2.54			1	0.015	0.056	
						1	3.7	
RhCl$_3$						310.2	198.8	
						(1.9)	(3.1)	
						1	3	

[a] See footnote to Table 1 with addition; fourth line presents atomic ratios with Rh as base.
[b] As-received, ground and unground samples.
[c] Batch for RhCl$_3$X, batch for Rh(NH$_3$)$_5$ClX and a blank ion exchanged sample.

Activation Reactions

For both $Rh(NH_3)_5ClX$ and $[Rh(NH_3)_5Cl]Cl_2$ there is very close agreement between the observed Rh $3d_{5/2}$, Cl $2p$ and N $1s$ B.E. In addition the Rh : N : Cl elemental ratio found for $Rh(NH_3)_5ClX$ is as expected for ion exchange of $[Rh(NH_3)_5Cl]^{2+}$ ions into the zeolite. Sodium loss measurements support the contention that ideal exchange has taken place. The Rh $3d_{5/2}$ B.E. of 310.2 eV was similar to that found earlier for $RhCl_3X$ (8) and it would appear that Rh(III) is present in both cases. A similar situation has been reported for $Rh(NH_3)_5ClY$ (10, 11).

It is important to note that all the samples of $Rh(NH_3)_5ClX$ examined here were found to exhibit significant time-dependent spectra with respect to the Rh $3d$ core lines. A comparison of spectra B and C in Fig. 1 reveals that the original Rh $3d_{5/2}$ line at 310.2 eV broadens asymmetrically towards lower B.E. during X-ray exposure for some time. No changes in the lines originating from elements in the support are seen. X-Ray induced decomposition at the Rh centres is clearly responsible and in this respect the $Rh(NH_3)_5ClX$ samples are very much more sensitive than the $RhCl_3X$ catalysts (8). Sample temperature during analysis is of importance. Thus $Rh(NH_3)_5ClX$ after vacuum treatment at 400°C for 0.5 h and analysis at the same temperature leads to a Rh $3d_{5/2}$ line at 308.2 eV. A similarly vacuum-treated sample analyzed at the lower temperature of $-60°C$ gives rise to a line at 309.9 eV. A clear difference in the N : Rh ratio (1.9 vs 4.2) was also apparent. A sample temperature of 25°C ensured that spectra reflected the initial state of the sample since decomposition rates were then sufficiently low.

Treatment of $Rh(NH_3)_5ClX$ with either nitrogen or oxygen at 400°C for 0.5 h (up to 23 h) led to no detectable change in the Rh $3d$ lines, although the N : Rh ratio drops to 2.4 (2.0). It would appear that during the loss of the associated ligands no change in oxidation state of the Rh occurs. After thermal treatment of $RhCl_3X$, Rh(III) is similarly retained but in this case there is an absence of associated Cl even in the untreated catalyst (8).

Under nitrogen at higher temperatures (600°C) rhodium metal is produced. The Rh $3d_{5/2}$ B.E. is at 307.3 eV and there is a fall in intensity compared with the original sample, indicating the occurrence of sintering (16). In addition No Cl $2p$ or N $1s$ lines are seen. Treatment with hydrogen at 340°C instead brings the Rh line to 308.2 eV. This is the same position as that obtained for the low B.E. peak produced during X-ray-induced decomposition under vacuum at 400°C and it seems likely that monovalent rhodium (compare Table 1) or zerovalent rhodium in a highly dispersed state is responsible. Core lines shifted to higher B.E. are commonly encountered if the metal particles concerned are extremely small, nearly atomically dispersed (17, 18). Although these shifts can be adequately explained by relaxation effects, chemical effects could also be of importance. For small aggregates of platinum or palladium, electron donation from metal to the support is indicated (19). It is significant that treatment of $RhCl_3X$ with hydrogen at the same temperature, although admittedly for a slightly longer period, brought the Rh $3d_{5/2}$ line to 307.8 eV (8). The lower B.E. in this case is closer to that expected for bulk metallic rhodium and so it seems that the final dispersion is much lower in this catalyst.

This in turn implies that the initial dispersion of the rhodium compound may also be lower and that some degree of agglomeration is already to be found in the initial catalyst. According to the elemental compositions obtained by ESCA (Table 2), the Rh : Si ratios are 0.017 and 0.075 for $Rh(NH_3)_5ClX$ and $RhCl_3X$, respectively. The figure for $Rh(NH_3)_5ClX$ is close to that predicted on the basis of the bulk composition of the material as expected for homo-

geneous incorporation of the cation into the zeolite during exchange. For $RhCl_3X$, however, the surface concentration of rhodium is clearly larger than expected and a substantial introduction of rhodium into the zeolite by "impregnation" at the outer geometric surfaces of the individual crystallites rather than by bulk exchange seems likely to be responsible. This is not entirely unexpected when using rhodium trichloride rather than a well-defined cationic species. For $Rh(NH_3)_5Cl$-mordenite (Table 2) the Rh : Si ratio deviates from that expected on the basis of bulk composition to a slightly greater degree than found with zeolite X but incorporation of rhodium largely by homogeneous ion exchange appears likely, also considering Rh : N : Cl ratios.

Returning to $Rh(NH_3)_5ClX$, the N 1s B.E. at ca. 400 eV is as expected and the value is relatively insensitive to catalyst pretreatments. There are, however, significant shifts in the Cl $2p$ B.E. during the various thermal treatments. Originally at 198.7 eV and close to the value of 198.5 eV found for $[Rh(NH_3)_5Cl]Cl_2$, there are increases of between 0.5 and 1.0 eV after heating. Since the spread in the Cl $2p$ B.E. seen for example for a collection of 42 different rhodium compounds is about 1.1 eV (20) it seems likely that the changes observed here are largely attributable to alterations in the chemical environment of the chlorine ligands as water and ammonia are removed from the surface. Bridging chlorine atoms usually possess B.E. some 0.5 to 1.2 eV higher than terminal atoms (21) but it is not clear whether the formation of such bridges, by for example interaction between neighbouring rhodium centres in $Rh(NH_3)_5ClX$ at elevated temperatures, is responsible for the shifts observed with this catalyst. Finally it should be added that in addition to the above-mentioned effects, the loss of water during activation removes a situation where active sites and the pore structure are blocked by water molecules.

Carbonylation Reactions

The changes induced by contact of the Rh zeolites with carbon monoxide are followed by monitoring the Rh $3d_{5/2}$ core line. Attempts to supplement these measurements by observing the C $1s$ and O $1s$ core lines for adsorbed CO failed due to difficulties in resolving the individual peaks from the large contributions already present in the background spectrum at these positions arising from carbon contamination and lattice (support) oxygen, respectively.

Treatment with carbon monoxide at 50 or 100°C leads to no changes in the Rh $3d_{5/2}$ B.E. (Table 1 and Figure 1), although infrared spectroscopic measurements clearly indicate the formation of rhodium carbonyl units under such conditions (3). Such a result is consistent with data obtained by ESCA for adsorption of CO on $RhCl_3X$ (8) and a further example is provided by recent studies on the recarbonylation of rhodium clusters on alumina (22). The lack of shift in the Rh $3d_{5/2}$ line is however at variance with the results of Primet et al. for $Rh(NH_3)_5ClY$ (10, 11). These authors provide evidence for the formation of $Rh(I)(CO)_2$ species resulting from exposure of the Rh(III)-containing zeolite to CO since there is an accompanying change in the position of the Rh $3d_{5/2}$ line from 310.8 to 308.1 eV. A possible explanation is to be found in their observation that the formation of Rh(I) carbonyls is favoured by the presence of water in the zeolite. In our electron spectrometer no water had been added to the system and the outgassing extent is such that ultimate vacua of about 10^{-9} Torr are attained. As seen from Table 1 and Fig. 1, if the carbon monoxide used is saturated with water then the Rh $3d_{5/2}$ line is indeed shifted down to 308.3–308.4 eV. In the infrared work (3) higher ultimate pressures are encountered and the degree of dehydration and dehydroxylation of the zeolite is correspondingly less. Even so some forma-

tion of Rh(III) carbonyls has been suggested in the case of $Rh(NH_3)_5ClX$ (3). Also notable is that Rh(III) was more fully coverted at the higher temperature of treatment in CO.

Treatment of $Rh(NH_3)_5ClX$ with a mixture of carbon monoxide and methyl iodide is also without effect on the Rh $3d_{5/2}$ B.E. but adsorption of iodine has occurred giving rise to new signals in the spectrum. The situation is similar for $RhCl_3X$ but different I : Rh ratios are observed. The ratio is clearly higher for $Rh(NH_3)_5ClX$ (1.7 rather than 0.3) and despite fairly large uncertainties in these values, attributable to time dependency, this may well reflect a higher concentration of rhodium sites available for formation of carbonylation centres on the ammine-exchanged catalyst. However, CO treatment alone did not yield a C $1s$ (CO) peak of corresponding intensity implying that either CH_3I activates the Rh centres and/or it chemisorbs on the support in addition. IR data indicate that CH_3I itself is not present to any significant extent under these conditions (8). Acetyl build-up on the support (11) might provide an explanation of the results obtained.

Effect of the Support

Turning first to the elemental ratios in Table 2 it is seen that as received, ground and unground $RhCl_3X$ yields identical data which is also the case for blank ion exchanged and various batches of NaX. All values are also close to those for $Rh(NH_3)_5ClX$, i.e., within the experimental error estimated as 10%. However, there are some discrepancies compared with the theoretical compositions, especially for Al, which is somewhat lower than expected. In earlier measurements on $RhCl_3X$ (8) these differences were larger. However, the influence of the *Brehmsstrahlung*-induced Al KLL Auger peaks was not estimated at that stage. Since the earlier work was not performed with the same anode and window as the present, it is suggested that the

Brehmsstrahlung effect was larger then, in conformity with the differences found.

In Table 2 it is seen that the Rh $3d_{5/2}$ B.E. for $RhCl_3/SiO_2$ and $RhCl_3/SnO_2$ lying at 308.6 and 308.2 eV respectively are significantly lower than that for $RhCl_3/MgO$ at 309.8 eV which is close to the values found for the rhodium zeolites. In attempting to assign formal oxidation states using these B.E. a comparison with literature data on various rhodium complexes is made (Table 1) and it is suggested that in $RhCl_3/MgO$ and in the rhodium zeolites Rh(III) is present, whereas for $RhCl_3/SiO_2$ and $RhCl_3/SnO_2$ Rh(I) appears more likely. For $RhCl_3/SnO_2$, a treatment in air at 600°C did not result in any increase in the Rh $3d_{5/2}$ B.E. indicating that no oxidation of the rhodium species took place. The Rh(I) state is therefore apparently rather stable and this may well reflect the occurrence of some specific interaction between rhodium and support. This interaction may in some measure account for the lack of carbonylation activity of these samples, though for SiO_2 as support an additional factor has to be taken into account. Crystals of the rhodium salt can be detected even with an optical microscope and the signals obtained by ESCA are of very low intensity. A rather weak specific interaction between rhodium and the support is indicated and this is associated with a relative ease of decomposition of the rhodium salt during thermal treatment. Differences in preparational procedures can perhaps account for the observations made by others that silica-supported rhodium can exhibit some carbonylation activity (5) albeit at a much lower level than that found for rhodium zeolites (3, 7).

For those materials containing Rh(III) only two are catalytically active and so it would appear that the initial presence of Rh in this oxidation state may be a necessary but not sufficient requirement for the development of activity in carbonylation.

Clearly, the active $RhCl_3X$ only contains

minor amounts of chlorine, whereas the inactive $RhCl_3/MgO$ contains much of the chlorine originally present. Possibly the positive effect of the zeolite is that the Rh ions are bonded in a flexible way with only hydroxyl and water ligands that, to some extent, are easily removed during the activation procedure, forming coordinatively unsaturated centres capable of bonding CO and CH_3I molecules for reaction. The mordenite-support catalyst may be inactive because of severe steric restrictions imposed by the relative small dimensions of the channels present but more work is required before a definite conclusion can be made. Certainly the present data do not indicate any other physico-chemical reason for the behaviour.

Suggestions that Rh(0) may be responsible for *carbonylation* activity of rhodium zeolites (26) appear to be premature in view of the lack of direct evidence for the state of rhodium in working catalysts, and particularly in view of the important role played by Rh(I) complexes which has been established for homogeneous catalysis. Furthermore, that Rh(0) provides the seat of *catalytic action in general* for rhodium zeolites seems very unlikely, considering in particular the observations of Okamoto *et al.* (12).

The evidence for the higher dispersion of rhodium in $Rh(NH_3)_5ClX$ seems fairly strong but even so it is felt unlikely that the very large difference in specific activities of $Rh(NH_3)_5ClX$ and $RhCl_3X$ can be ascribed merely to a greater concentration of sites in the former. It would appear that the location of the rhodium centres within the zeolite cages rather than at the external surface of the crystallites may be of critical importance. The pronounced electrostatic fields within the zeolite lattice may have a part to play in assisting in the formation of suitable rhodium centres and/or accelerating the rate of formation of acetyl units by dissociative adsorption of methyl iodide which by analogy with homogeneous catalysis seems to comprise the rate-determining step (1, 3, 6, 7). A further function of the

zeolite may be to assist in hydrolytic decomposition of the acetyl intermediates formed (11). It is therefore possible to regard the zeolite as a "solid-solvent" for the components of the carbonylation reaction.

The acid–base properties of oxide surfaces appear to be important in helping to explain relatively small variations in the rates of carbonylation for certain supported catalysts (5) but there can be little doubt that the most active catalysts by far are those based on type X or Y zeolites. This feature is even more intriguing since zeolites are typically associated with incorporated cationic species whereas methanol carbonylation at least in solution proceeds most rapidly with anionic complexes (27).

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