

Zeolite Supported Rhodium Carbonyls from $\text{Rh}(\text{allyl})_3$ and Their Use as 1-Hexene Hydroformylation Catalysts

DENNIS F. TAYLOR, BRIAN E. HANSON* and MARK E. DAVIS*

Department of Chemistry and Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061, U.S.A.

(Received August 21, 1986)

Abstract

Rhodium has been introduced to protonated zeolite Y (HY) and partially protonated zeolite Y (5% HNaY) as the tris-allyl complex, $\text{Rh}(\text{C}_3\text{H}_5)_3$. The resulting zeolite, RhHY or RhNaY , may be reduced in CO to yield $\text{Rh}(\text{CO})_2^+$ or $\text{Rh}_6(\text{CO})_{16}$ depending on the reaction conditions. Reaction with phosphines suggests that rhodium lies both within the zeolite framework and on the zeolite surface. When the zeolite supported phosphine complexes are used as solution hydroformylation catalysts, all of the observed activity appears to come from the solution phase as rhodium is leached from the support.

Introduction

Rhodium-containing zeolites have received a great deal of attention as carbonylation [1], hydrogenation [2], and hydroformylation [3–6] catalysts. For the carbonylation of alcohols, selectivity is not generally a problem and for this reaction zeolites have provided a convenient support. In the hydrogenation and hydroformylation of alkenes by rhodium zeolites, some selectivity enhancement was anticipated based on shape selectivity by the zeolites [2, 4]. This will only be realized, however, if the catalytically active sites are contained completely within the zeolite pore structure. Since it is unlikely that all active sites will be within the zeolite, surface poisons have been employed in the liquid phase hydrogenation of olefins [2]. In this manner modest selectivity enhancements have been obtained [2c].

For the gas phase hydroformylation of propylene by rhodium-containing X and Y zeolites, selectivities of normal-to-isobutyraldehyde in the range of 1.8–2.5 are observed. However, these are interpreted as due to modification of the rhodium rather than to shape selectivity by the zeolite since the faujasite pores are large compared to propylene, CO and H_2 .

Also similar selectivities are observed for silica supported rhodium [3c]. Furthermore, evidence from poisoning experiments locate the bulk of the catalytically active sites on the surface of the zeolite particles for these catalysts [3a].

When the hydrogenation or hydroformylation reaction is performed in the liquid phase by a zeolite supported rhodium catalyst, elution of the metal from the support to give a homogeneous catalyst is a serious problem. On silica gel or polymeric supports, metal elution is minimized by using chelating phosphines to attach the metal to the support [7]. With zeolites as a support, metal elution may be minimized if the complex lies within the cages of the zeolite and is too large to come out through the pores [3, 6].

In a previous study [4] on the activity of rhodium zeolites generated by cation exchange for liquid phase 1-hexene hydroformylation, it was proposed that three different types of active sites were observed: (i) rhodium in solution, (ii) rhodium on the surface of the zeolite particles, and (iii) rhodium trapped within the supercages of the zeolite. However, more recent experiments from our laboratories suggest that all of our reported activity for 1-hexene hydroformylation by cation-exchanged rhodium faujasites comes from rhodium that has either migrated to the surface of the zeolite or leached into solution [8].

Recent work by Schwartz *et al.* [2a, b] demonstrates that incorporation of rhodium onto partially protonated zeolites as the tris-allyl complex, $\text{Rh}(\text{C}_3\text{H}_5)_3$, places a very high percentage of the rhodium within the zeolite pore system. We have generated similar materials in our laboratory and have studied them as catalysts for the liquid phase hydroformylation of 1-hexene as well as by infrared spectroscopy in their reactions with CO and phosphines. These experiments are consistent with the location of the rhodium both within the zeolite pores and on the surface; however, under hydroformylation conditions, rhodium is rapidly lost from the zeolite.

*Authors to whom correspondence should be addressed.

Experimental

The zeolites NaY and NH₄Y were obtained from Strem Chemical Company and treated as described below. Tris-allyl rhodium(III) was synthesized by literature methods from RhCl₃·3H₂O (Johnson Matthey). Pentane was distilled from NaK-benzophenone prior to use. Rhodium was introduced to protonated forms of the zeolite using the methods described by Schwartz *et al.* [2a, b]. Unless otherwise indicated, all operations were performed under N₂ on a Schlenk Line or in a Vacuum Atmospheres Drybox.

The phosphines, PEt₃, PMe₂Ph, P(nBu)₃ and PMePh₂, were obtained from Pressure Chemical Company. All infrared spectra were recorded on either a Nicolet MX1 or Nicolet 5DXB Fourier Transform Infrared Spectrometer. Rhodium analysis was performed by acid digestion of the zeolites followed by atomic absorption analysis.

Preparation of RhHY

The ammonium form of zeolite Y was heated to 450 °C for 3.5 h in the presence of flowing helium to generate the hydrogen form of the zeolite, HY. Rhodium was then introduced by slurring approximately 7.5 g of HY with 1.0 g of tris-allyl rhodium in 100 ml of pentane. Stirring was continued overnight. The zeolite, which had decolorized the pentane solution, was filtered under N₂, dried at room temperature under vacuum, and stored under nitrogen.

Preparation of RhNaY

Partially protonated Y zeolite was prepared by slurring 25 g of NaY with 1.9 g of NH₄Br at 75 °C for 48 h. The zeolite was washed with distilled water until no bromide was detected by AgNO₃. The zeolite was heated to 475 °C under flowing helium for 3 h. The amount of protonation was determined by reaction of the anhydrous HNaY zeolite with methyl-lithium and observation of the amount of methane liberated. Typically, 4 to 6% of the cation exchange capacity of the zeolite was present as H⁺. This zeolite was then slurried in pentane with tris-allyl rhodium to give a rhodium loading corresponding to the total proton content of the zeolite. The rhodium zeolite, RhNaY, was stored under nitrogen.

Carbonylation of the Rhodium Zeolites

In a typical reaction 150 mg of the RhNaY zeolite was loaded into a glass reactor which was pressurized to 2 atm under flowing CO and then heated to 125 °C. The carbonylation was carried out for 4 h. The reactor was then transferred to a glove box in order to prepare infrared samples as either a KBr pellet or a nujol mull.

Phosphine Reactions

Reactions with liquid phosphines were performed in a nitrogen filled long-necked flask. A small amount of the carbonylated rhodium zeolite was placed in the bottom of the flask. An amount of phosphine, in a ratio of 9 equivalents phosphine per equivalent rhodium, was syringed into the neck of the flask. The phosphine vapor and zeolite were allowed to react overnight. The reaction with triphenylphosphine was performed by dry mixing the carbonylated rhodium zeolite and triphenylphosphine, in a molar ratio of 6 phosphines per rhodium, in a mortar and pestle under N₂. The infrared spectrum was monitored over a period of 4 days.

Catalyst Preparation and 1-Hexene Hydroformylation

The hydroformylation catalysts were prepared as described above by the reaction of tris-allyl rhodium with proton sites on HNaY. The rhodium zeolites were further reacted with phosphines prior to hydroformylation. The zeolite was placed in a flask with glass wool in the neck. Phosphine was syringed onto the wool in a molar ratio of 9 phosphine per rhodium. After reacting with the vapor the catalysts were loaded into a Parr Mini Reactor under nitrogen. The reactor was then charged with a dry, degassed solution of 5 ml 1-hexene in 45 ml of toluene and pressurized to 300 psig with a 1:1 mixture of hydrogen and carbon monoxide. The reactor was heated either to 50 °C or to 100 °C with constant stirring. Reaction times of 14 h were used unless otherwise indicated. Products were analyzed by gas chromatography.

In each case, rhodium analysis was performed on the liquid phase after hydroformylation. The zeolite was removed from the liquid by filtration either after the reactor had cooled to room temperature or while it was still hot. In some cases, to test for homogeneous activity, the liquid phase was returned to the Parr bomb with fresh 1-hexene in the absence of zeolite. The reactor was then repressurized and reheated to reaction temperature for an additional 14 h. Likewise, in some cases the solid catalyst was returned to a clean reactor to test for continued activity.

Results and Discussion

Figure 1 shows the infrared spectra obtained after carbonylation of RhHY at 2 atm pressure CO. Trace A shows the spectrum obtained when the carbonylation is performed under anhydrous conditions. Four bands are observed in the terminal carbonyl region at 2111, 2090, 2044 and 2020(sh) cm⁻¹. In several laboratories [1–6] similar infrared spectra have been obtained from cation exchanged rhodium zeolites. These spectra have been interpreted in

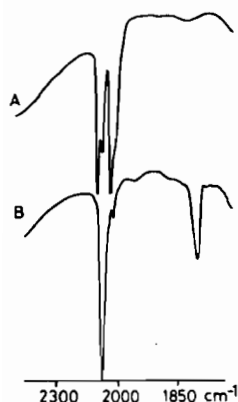


Fig. 1. A: Infrared spectrum of RhHY after reduction in CO at 2 atm and 125 °C. B: The same sample as in A after addition of H₂O.

several ways, including the presence of rhodium dicarbonyl dimers, two different rhodium dicarbonyl complexes with different types of oxygen donor ligands, and the presence of rhodium dicarbonyls both on the surface and in the interior of a zeolite particle. Trace B shows the spectrum of a sample that was treated first as in 1A, then subjected to water vapor under CO pressure. Clearly, this sample does not contain any rhodium dicarbonyl within the limits of detection by infrared spectroscopy. The bands observed (2081, 2025 and 1801) are very similar to Rh₆(CO)₁₆ [3]. Direct addition of Rh₄(CO)₁₂ or Rh₆(CO)₁₆ to zeolite Y gives a similar spectrum and has been interpreted to be due to Rh₆(CO)₁₆ on the surface of the zeolite particle. The need for water for the synthesis of Rh₆(CO)₁₆ from Rh(CO)₂⁺ on zeolite Y [3b] and silica [9] has been demonstrated previously.

Carbonylation of RhNaY at 2 atm CO yields a spectrum similar to that obtained for RhHY. Trace A of Fig. 2 shows the results of direct carbonylation of RhNaY. Four bands are observed in the terminal region at 2109, 2098, 2035 and 2016 cm⁻¹. In addition there are bridging bands at 1827 and 1765 cm⁻¹. The bulk of the rhodium appears to be present as rhodium dicarbonyls, although the bridging bands indicate the presence of some clusters perhaps Rh₄(CO)₁₂ and Rh₆(CO)₁₆ [3b]. Addition of water vapor to this sample converts all of the rhodium species on the zeolite to clusters. (Traces of water are observed in 2A as indicated by the H₂O bending mode at 1640 cm⁻¹. This is either not removed in the catalyst pretreatment or adventitiously scavenged during subsequent synthesis steps.) Thus trace B of Fig. 2 shows bands at 2089, 1800 and 1765 cm⁻¹. It has been suggested previously that a spectrum of this type with bridging bands at ~1770 cm⁻¹ is consistent with Rh₆(CO)₁₆ within the supercage of the zeolite [3b, 6]. The higher frequency bridging band, 1800 cm⁻¹, is more consistent with the rhodium

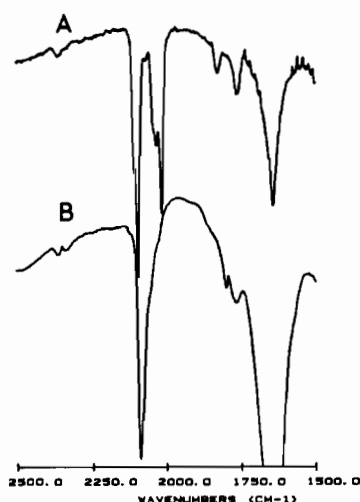


Fig. 2. A: Infrared spectrum of RhNaY after reduction in CO at 2 atm and 125 °C. Residual water is evident from the H₂O bending mode at 1640 cm⁻¹. B: The same sample as in A after addition of H₂O.

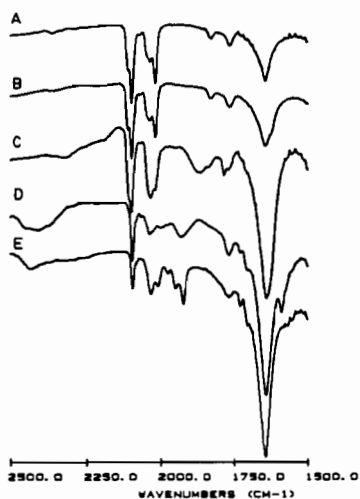


Fig. 3. Infrared spectra for the reaction of RhNaY with CO and various phosphines. The spectra are scaled in the carbonyl region which results in the water bending mode to appear to increase in going from A to E. A: Infrared spectrum of RhNaY after reduction in CO at 2 atm and 125 °C (compare 2A). B: The same sample as in A after addition of PMePh₂. C: The same sample as in A after addition of P(nBu)₃. D: The same sample as in A after addition of PMe₂Ph. E: The same sample as in A after addition of P(Et)₃.

cluster on the surface. This experiment suggests that rhodium clusters are formed both within the zeolite cages and on the surface.

The reaction of rhodium carbonyls on RhNaY with phosphines lends further support for the location of rhodium both within the zeolite pores and on the surface. Figure 3 presents the infrared spectra for carbonylated RhNaY with various phosphines; trace

A shows the result of carbonylation (compare with trace A, Fig. 2) while traces B–D show the infrared spectra after reaction with PMePh_2 , $\text{P}(\text{n-Bu})_3$, PMe_2Ph and PEt_3 , respectively.

Addition of PMePh_2 to carbonylated RhNaY results in no change in the infrared spectrum (compare traces A and B). Therefore the supported rhodium carbonyls are either inaccessible to the phosphine or simply do not react with the phosphine at room temperature. Methylidiphenylphosphine is too large ($\sim 9 \text{ \AA}$ cross section) to penetrate the zeolite pores thus it is likely that this phosphine will not reach rhodium carbonyls within the zeolite. Characteristic phosphine bands are not seen in the infrared for this sample, thus it is also possible that too little of the phosphine reached the zeolite to react.

Tri-*n*-butylphosphine reacts with some of the supported carbonyls. Trace C in Fig. 3 shows that the 2088 and 2016 cm^{-1} bands have diminished in intensity while a new broad band appears at 1860 cm^{-1} . This phosphine is comparable in cross-sectional diameter ($\sim 8.4 \text{ \AA}$) to the kinetic pore diameter of the zeolite. Thus, it is possible for $\text{P}(\text{nBu})_3$ to react with rhodium carbonyls at or near the surface.

The smaller phosphines PMe_2Ph and PEt_3 react with the carbonylated RhNaY to remove all traces of the dicarbonyl, traces D and E in Fig. 3. However, bands remain at 2095 and 1773 cm^{-1} which suggests that even these small phosphines are not able to react with the species assigned as $\text{Rh}_6(\text{CO})_{16}^*$. This, alone,

*IR bands at 2095 and 1770 cm^{-1} have previously been assigned to $\text{Rh}_6(\text{CO})_{16}$ inside the zeolite in cation exchanged rhodium zeolites. Also this cluster reacts with PMe_2Ph at 120 °C [3b].

does not allow us to unambiguously assign the location of the cluster since it is possible that the cluster is on the surface of the zeolite yet will not react with any of the phosphines. We note however that many phosphines react rapidly with $\text{Rh}_6(\text{CO})_{16}$ under fairly mild conditions (40–45 °C) to yield substituted rhodium clusters and dinuclear rhodium complexes. Thus $\text{Rh}_6(\text{CO})_{16}$ on the surface of a zeolite particle should show evidence of reaction over a 14 h period. If, on the other hand, the cluster occupies a supercage then there may not be sufficient room to allow a substitution reaction to occur. To test this the reaction was performed at 45 °C with PMe_2Ph . Even at this elevated temperature the $\text{Rh}_6(\text{CO})_{16}$ was left unchanged over a reaction time of 14 h. Thus we conclude that $\text{Rh}_6(\text{CO})_{16}$ within the zeolite is inert towards phosphines at temperatures below 50 °C. Finally we note that $\text{Rh}_6(\text{CO})_{16}$ unambiguously located on the surface of faujasites reacts with both large and small phosphines at room temperature [10].

Liquid Phase Hydroformylation of 1-Hexene

The results for the liquid phase hydroformylation of 1-hexene at 50 and 100 °C are summarized in Tables I and II. All catalytic reactions were performed on two preparations of RhNaY ; these analyzed for a rhodium content of 1.9 and 2.0 weight percent. Reactions were run on blank zeolite, RhNaY without phosphine, and RhNaY with various phosphines. The phosphine was always added to the zeolite in a separate flask prior to the catalytic run or any exposure of the sample to carbon monoxide. No additional phosphine was added to the reactor.

TABLE I. Hydroformylation of 1-Hexene at 50 °C^a

Run	Phosphine	Rhodium loading	Reactor charge	Conversion ^b	Selectivity ^c	<i>n/b</i>	Rh elution ^d
1		1.9%	0.54 ^g	52	53	2.0	0.5%
2		2.0	0.51	87	63	2.2	6.3
3	PEt_3	1.9	0.78	3	41	2.4	e
4	PEt_3	2.0	0.55	0	0	0	e
5	PMe_2Ph	1.9	0.53	2	18	2.1	e
6	PMe_2Ph	2.0	0.60	0	0	0	e
7	PMePh_2	1.9	0.58	50	75	2.2	0.04
8	PMePh_2	2.0	0.53	100	81	1.4	10
9	$\text{P}(\text{n-Bu}_3)$	1.9	0.72	11	77	2.4	1.9
10	$\text{P}(\text{tBu}_3)$	1.9	0.71	87	68	2.0	1.6
11	$\text{P}(\text{tBu}_3)$	2.0	0.53	23	65	2.3	4.5
12	PPh_3	1.9	0.71	24	89	2.8	0.04
13 ^f		0.0	0.50	8.5 ^g	0		
14 ^f	PEt_3	0.0	0.64	0	0		

^aInitial pressure 300 psig CO/H_2 ; 1/1. ^bConversion: total products/initial charge of 1-hexene (the observed products were heptanal, 2-methyl-hexanal, 2 ethyl-pentanal, *cis* and *trans* 2-hexene, and *cis* and *trans* 3-hexene). ^cSelectivity: hydroformylation products/total products. ^dPercentage of charged rhodium found in solution by analysis. ^eNo rhodium detected by atomic absorption analysis. ^fBlank zeolite was 5% HNaY . ^gIsomerization products only were observed; 2-hexene and 3-hexene.

TABLE II. Hydroformylation of 1-Hexene at 100 °C^a

Run	Phosphine	Rhodium loading	Reactor charge	Selectivity	Conversion	<i>n/b</i>	Rh elution
1	PEt ₃	2.0	0.59	90	100	2.3	1.6
2a	PEt ₃	2.0	0.57	95	98	2.3	1.0
2b ^b	Solution from a			99	74	1.8	
3a	PEt ₃	2.0	0.52	100	99	2.3	^e
3b ^d	Solution from 3a			99	87	0.9	
4a	PEt ₃	2.0	0.49	98	75	1.6	^c
4b ^d	Solution from 4a			99	83	0.8	
4c ^e	Solid from 4a			99	84	0.4	
5 ^e	PEt ₃	2.0	0.50	100	84	0.6	

^aInitial pressure 300 psig CO/H₂; 1/1. ^bFiltered hot under N₂. ^cRhodium elution not measured but homogeneous activity tested. ^dSolution exposed to air. ^eSolid catalyst exposed to air.

From the results in Table I it is evident that there appears to be some correlation between conversion and rhodium elution. In particular for runs 3–6 in which no rhodium is detected in solution the conversion is either very small or not observable. For each of these runs the phosphine is small enough to penetrate the zeolite pores. Thus it is reasonable to expect the phosphine to complex the rhodium within the zeolite framework. (Note that for the materials used as catalysts the phosphines are added prior to carbonylation, thus there are no Rh₆(CO)₁₆ clusters present on the zeolite which may fail to react with the phosphine.) Furthermore the lack of rhodium in solution indicates that these complexes are indeed too large to move out of the zeolite. The unfortunate additional fact is that at 50 °C virtually no activity for hydroformylation is observed for these materials. The reason for this is not clear since the reactant and product molecules are certainly small enough to pass through the zeolite pores. One possibility is that the phosphine serves to poison intrazeolitic rhodium. This appears unlikely in view of the abundance of rhodium phosphine complexes which are active for hydroformylation under mild conditions. Another possibility is that the phosphine serves to block the pores of zeolite to passage of the olefin.

Table II shows the results for hydroformylation of 1-hexene at 100 °C using triethyl phosphine which appears to bind the rhodium to the zeolite at 50 °C (Table I). One obvious result of raising the temperature to 100 °C is that the conversion for all catalyst preparations is greater than 90%. Also as seen for reactions 1 and 2, rhodium elution as determined by filtering the reaction solutions while still hot, is significantly higher than for the same preparations at 50 °C. Furthermore the filtered solutions also show hydroformylation activity similar to that observed for the original solid (compare 2a and 2b). In some cases, 3b and 4b, the filtered solutions show significantly lower *n/b* ratios than the parent solid catalyst. For

both these solutions however the filtrate had been exposed to air. Also the filtered solid, 4c, shows reduced selectivity after exposure to air. Finally catalyst 5 prepared as for 1, 2, 3 and 4 but intentionally exposed to air prior to charging the reactor also shows a reduced selectivity. One possible explanation for the reduced selectivity is oxidation of the triethyl phosphine which would lead to activity via binary rhodium carbonyls. Binary rhodium carbonyls are active for hydroformylation and typically show much lower *n/b* ratios than phosphine substituted rhodium complexes when compared at high conversion [4]. The major conclusion to be drawn from this data is that the observed activity must be attributed to homogeneous rhodium complexes. This is best demonstrated by reactions 2b, 3b and 4b in Table II which were run on the filtrates.

Acknowledgements

We thank the NSF for support of this work (CPE 8216296). Additional support was provided by the Jeffress Memorial Trust. We gratefully acknowledge a generous loan of RhCl₃·3H₂O from Johnson Matthey.

References

- (a) B. Christenson and M. S. Scurrill, *J. Chem. Soc., Faraday Trans. 1*, 73, 2036 (1977); (b) 74, 2313 (1978); (c) S. L. T. Anderson and M. S. Scurrill, *J. Mol. Catal.*, 18, 375 (1983); (d) J. Yamanis, K. C. Lien, M. Caracotsico and M. E. Powers, *Chem. Eng. Commun.*, 11, 355 (1981); (e) J. Yamanis and K. C. Yang, *J. Catal.*, 69, 498 (1981); (f) T. Yashima, Y. Orikasa, N. Takahashi and N. Hara, *J. Catal.*, 59, 53 (1979); (g) N. Takahashi, Y. Orikasa and T. Yashima, *J. Catal.*, 59, 61 (1979).

- 2 (a) T. N. Huang and J. Schwartz, *J. Am. Chem. Soc.*, **104**, 5244 (1982); (b) T. N. Huang, J. Schwartz and N. Kitajima, *J. Mol. Catal.*, **22**, 389 (1984); (c) D. R. Corbin, W. C. Seidel, L. Abrams, N. Herron, G. D. Stucky and C. A. Tolman, *Inorg. Chem.*, **24**, 1800 (1985).
- 3 (a) E. J. Rode, M. E. Davis and B. E. Hanson, *J. Catal.*, **96**, 563 (1985); (b) **96**, 574 (1985); (c) M. E. Davis, E. J. Rode, D. F. Taylor and B. E. Hanson, *J. Catal.*, **86**, 67 (1984); (d) E. J. Rode, M. E. Davis and B. E. Hanson, *J. Chem. Soc., Chem. Commun.*, 1477 (1985).
- 4 M. E. Davis, P. Butler, J. Rossin and B. E. Hanson, *J. Mol. Catal.*, **31**, 385 (1985).
- 5 (a) N. Takahashi and M. Kobayashi, *J. Catal.*, **85**, 89 (1982); (b) H. Arai and H. Tominaga, *J. Catal.*, **75**, 188 (1982).
- 6 E. Mantovani, N. Palladino and A. Zanobi, *J. Mol. Catal.*, **3**, 285 (1977/78).
- 7 J. P. Collman, J. A. Belmont and J. I. Brauman, *J. Am. Chem. Soc.*, **105**, 7288 (1983).
- 8 M. E. Davis, J. Schnitzer, J. A. Rossin, B. E. Hanson and D. Taylor, *J. Mol. Catal.*, **39**, 243 (1987).
- 9 A. Theolier, A. K. Smith, M. Leconte, J. M. Basset, G. M. Zanderighi, R. Psaro and R. Ugo, *J. Organomet. Chem.*, **191**, 415 (1980).
- 10 B. E. Hanson, M. E. Davis, D. Taylor and E. Rode, *Inorg. Chem.*, **23**, 52 (1984).