Synthesis of Rhodium Zeolite A

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A novel procedure for the synthesis of rhodium containing zeolite A is presented; rhodium exchanged zeolite A crystals are added to synthesis gels to produce zeolite A with intracrystalline rhodium.

We have been investigating rhodium zeolites as catalysts for the hydroformylation of alkenes in the gas and liquid phases.[1] The advantages of heterogenizing rhodium or any catalytic metal within a zeolite pore structure are twofold; immobilization, and possible reaction selectivity enhancements due to molecular sieving. Shannon et al.[2] showed that rhodium can be cation exchanged into large-pore zeolites such as the synthetic faujasite NaY and mordenite but not into zeolite A. These results were determined by evaluating the surface-to-bulk rhodium content using Rh/Si from X-ray photoelectron spectroscopic (X.P.S.) and chemical analysis (C.A.). For RhNaA, the X.P.S./C.A. ratio for Rh/Si was 60. Also, the (Si

+ Al)/O ratio from X.P.S. was 0.23 [ideal structure of NaA gives (Si + Al)/O = 0.5] indicating an enrichment in surface oxygen. Shannon et al.[2] concluded that during the exchange of aqueous $RhCl_3$ with NaA (hydrated rhodium species are too large to enter the zeolite) the rhodium is deposited on the external surface via hydrolysis to form a 'Rh-oxy-hydroxy hydrate complex'.[2] To date, Kuehl[3] has provided the only example of a rhodium containing type-A zeolite. Kuehl crystallized zeolite alpha (high-silica-containing type-A zeolite) in the presence of penta-ammine(chloro)rhodium chloride (rhodium salt added to the synthesis gel). From the hydrogenation of linear and branched hydrocarbons, it was shown that extracrystalline as well as intracrystalline rhodium existed. However, since the branched chain hydrogenation activity was low, the catalysis was predominantly intracrystalline. Here we disclose a novel procedure for the synthesis of rhodium-containing zeolite A. Specifically, aqueous $RhCl_3$ is cation-exchanged with NaA and a portion of this material is placed in a zeolite A synthesis gel in order to 'seed' the synthesis of rhodium-containing zeolite A.

The synthesis procedures used in this study are described below. Pure NaA was synthesized from the following gel composition $3.5Na_2O \cdot Al_2O_3 \cdot 2.0SiO_2 \cdot 185H_2O$. Complete crystallinity was obtained in 4 h at 95 °C. Solid product samples were evaluated for degree of crystallinity by X-ray powder diffraction via comparison with an NaA standard. Visual inspections for product purity were also performed using scanning electron microscopy. Cation exchange of aqueous $RhCl_3$ for Na^+ in NaA was performed by dropwise addition of the rhodium solution into a 0.1 M NaCl slurry of NaA at 95 °C. After final addition of the rhodium solution the slurry was maintained at 95 °C overnight. Rhodium-containing zeolite A was synthesized by three procedures. First, our novel procedure: a portion of the aforementioned rhodium-exchanged NaA was added to a zeolite A synthesis gel with composition as previously described for the synthesis of pure NaA. The resulting gel was the charged into Teflon-lined autoclaves and heated to 95 °C at autogeneous pressure. Secondly, a procedure similar to that of Kuehl: $RhCl_3 \cdot xH_2O$ was added directly to the zeolite A synthesis gel with subsequent crystallizations steps maintained as before. Finally, pure NaA crystals and $RhCl_3 \cdot H_2O$ were added to the zeolite A synthesis gel with all other steps remaining the same. The RhNaA products were then exchanged at room temperature with $CaCl_2$. This exchange did not alter the rhodium content within the limits of our experimental error.

Table 1 shows the X.P.S. and C.A. (atomic absorption after acid digestion of the solid) data for the rhodium zeolite A preparations. The most obvious conclusion revealed by the data in Table 1 is that rhodium is incorporated into RhCaA by all the synthesis procedures while cation exchange locates rhodium on the external surface (X.P.S./C.A. ~1—5 vs. 60). The binding energy for rhodium $3d_{5/2}$ is approximately 310.5 eV for all our preparations indicating that rhodium is in the +3 oxidation state.[2] Also, the (Si + Al)/O ratios from X.P.S. analysis were 0.5 ± 0.1. Since the amount of superficial rhodium is very low in these preparations as compared to cation exchange, the possible enhancement of superficial oxygen content by the presence of rhodium oxide is probably not distinguishable by X.P.S. Therefore, we do not know whether the rhodium in our preparations is in the form of an oxide, cationically associated with the zeolite, or in both states. Since rhodium can form oxides, the equivalents of rhodium and calcium do not have to sum to the equivalents of aluminium. For our preparations, these equivalents were approximately the same but never strictly equal. The Rh/Si-X.P.S./C.A. ratio for the synthesis utilizing rhodium 'seed' crystals shows that the superficial concentration of rhodium is nearly equivalent to that of the bulk composition. When $RhCl_3 \cdot xH_2O$ is used as the rhodium source, the rhodium concentrates towards the surface of the crystals. Interestingly, the addition of NaA to the $RhCl_3 \cdot xH_2O$ synthesis gel causes
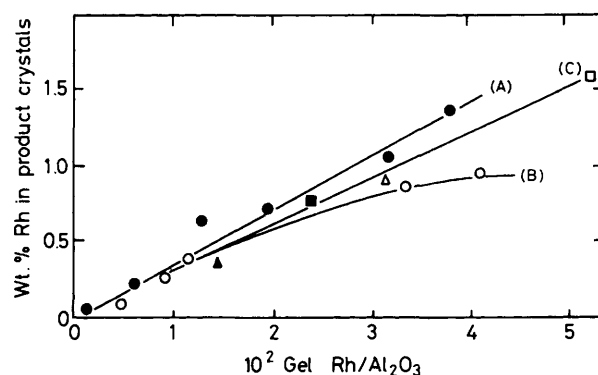

Figure 1. Rhodium utilization: (A) ●, $RhCl_3 \cdot xH_2O$; (B) ○, RhNaA (3.76 wt.% Rh); (C) RhNaA: ▲, 1.25 wt.% Rh; ■, 2.50 wt.% Rh; △, 3.25 wt.% Rh; □, 5.57 wt.% Rh.

Table 1. X.P.S. and C.A. data on zeolites.

Zeolite	Rhodium source	Wt.% Rh	Rh_{3d}/Si_{2p}		X.P.S./C.A.	Si_{2p}/Al_{2p}		X.P.S./C.A.
			X.P.S.	C.A.		X.P.S.	C.A.	
RhCaA	Cation exchanged RhNaA (3.76 wt% Rh)	0.96	0.0201	0.0153	1.31	0.83	1.16	0.72
RhCaA	$RhCl_3 \cdot xH_2O$	1.41	0.0869	0.0223	3.90	1.32	1.16	1.14
RhCaA	$RhCl_3 \cdot xH_2O$ (NaA also added to synthesis gel)	1.19	0.1140	0.0218	5.24	0.62	0.87	0.71
RhNaA[a]	Cation exchange of NaA with aqueous $RhCl_3$	1.25	1.33	0.022	60	0.90	1.00	0.90

[a] From ref. 2.

the superficial concentration of rhodium in the product crystals to increase. Thus, our rhodium 'seeding' procedure produces a superficial rhodium concentration which more closely resembles that of the bulk material than is possible by addition of $RhCl_3 \cdot xH_2O$ into the synthesis gel.

Figure 1 shows the utilization of rhodium for several syntheses. We use the term rhodium utilization to indicate the relationship between the amount of rhodium in the synthesis gel and that which ultimately is incorporated into the product crystals. Curve (A) is for syntheses utilizing $RhCl_3 \cdot xH_2O$. Curves (B) and (C) are for syntheses involving RhNaA 'seed' crystals. For (B), RhNaA crystals (3.76 wt.% Rh) were added to the synthesis gels in increasing amounts, while in (C), a constant amount of RhNaA was placed into the gels and the rhodium content varied from 1.25 to 5.57 wt.% Rh. The gel ratio Rh/Al_2O_3 does not include the Al_2O_3 contribution to the overall synthesis medium from the 'seed' RhNaA. No rhodium was detected in the filtrates of these syntheses indicating that all the rhodium added to the gels was ultimately incorporated into the product crystals. The rhodium material balances were 100 ± 5% for all syntheses shown.

Figure 1(A) shows that a linear relationship exists between the rhodium in the gel and the rhodium in the product crystals on addition of $RhCl_3 \cdot xH_2O$ to the gel. Since the amount of product crystals in each of these syntheses is relatively constant, a linear relationship is expected if all the gel rhodium is incorporated proportionally into product. When a variable amount of rhodium 'seed' is added to the synthesis gels, a linear utilization relationship is not obtained as can be seen in Figure 1(B). The observed curvature is the result of the 'seed'

crystals' contribution to the overall product yield. That is, in order to raise the rhodium content in the gel, increasing amounts of 'seed' (3.76 wt% Rh) were added to the gel which consequently resulted in the production of more RhNaA. To prove this result, a constant amount of 'seed' was added to the synthesis gels while the rhodium content was varied by changing the rhodium loading of the 'seeds.' The rhodium utilization results for this case are illustrated in Figure 1(C). Notice that a linear relationship is obtained. Again, this is due to the fact that a constant amount of product is synthesized.

We are attempting to elucidate further the chemistry of our synthesis procedure, and are extending our technique to produce intrazeolitic metals with zeolite A and other molecular sieves. Finally, we have observed shape selective hydroformylation from RhCaA.[4]

References

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