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Synthesis and Catalysis of Transition Metal-Containing Zeolite A

INTRODUCTION

Previously, we reported the synthesis of rhodium-containing zeolite A (*1*). Our procedure involved addition of rhodium-exchanged NaA to zeolite A synthesis gels in order to "seed" the synthesis of rhodium-containing zeolite A. By evaluating the superficial-to-bulk rhodium content using the Rh/Si ratio from X-ray photoelectron spectroscopy (XPS) and the chemical analysis from atomic absorption spectroscopy (CA), we concluded that the rhodium–zeolite A synthesized by our technique contained intrazeolitic rhodium (XPS/CA = 1.31). We also synthesized rhodium–zeolite A by addition of $RhCl_3 \cdot xH_2O$ to the synthesis gel. This procedure was similar to that first reported by Weisz and co-workers (*2–4*) for the synthesis of platinum-containing zeolite A. The XPS/CA for this material was 3.9 and therefore it must also contain intrazeolitic rhodium. Further characterizations of these materials are provided below, and these new data were used to direct improvements in our synthesis procedure.

The objective of this work is to disclose an improved procedure for the synthesis of transition metal-containing zeolite A. Rhodium and ruthenium salts are used to illustrate the technique. The CO-hydrogenation behavior of the transition metal-containing zeolite A materials are also provided in order to illustrate the catalytic ability of these new materials.

RESULTS AND DISCUSSION

The XPS and CA data for RhCaA materials previously synthesized (*1*) are provided in Table 1 along with similar data for $RhCl_3 \cdot xH_2O$-exchanged NaA. The X-ray diffraction patterns of materials A and B showed them to be highly crystalline. From visual inspections by scanning electron microscopy, material A possessed a broader range of crystal sizes (~0.5–8 μm) than did material B (~1–2 μm). This result is expected since the seeding of zeolite synthesis gels is known to broaden the distribution of crystal sizes in the product. To overcome this problem, we prepared an amorphous rhodium–aluminosilicate "seed." The amorphous seed was obtained by collecting and drying the solid product formed by reacting $RhCl_3 \cdot xH_2O$ with an aqueous slurry of sodium silicate and sodium aluminate (SiO_2/Al_2O_3 = 2) at 100°C for 1 h. The addition of the amorphous rhodium–aluminosilicate seed to the gel composition previously reported (*1*) resulted in product rhodium–zeolite A with a XPS/CA of 0.57 (after exchange with $CaCl_2$). Complete details of the synthesis are available (*6*). Visual inspection of this material (D) showed that the crystal size was very nearly uniform at approximately 1–2 μm.

Electron microprobe analyses of materials B and D were performed in order to ascertain the extent of rhodium homogeneity. The rhodium content of material D appears to vary from crystal to crystal. Interestingly, material B is uniform in rhodium content to within the limits of our detectability when scanning from crystal to crystal. However, mixed with the crystals of material B are submicron particles of rhodium oxide. Rhodium oxide is probably formed quite readily from $RhCl_3 \cdot xH_2O$ and the basic zeolite A gel. Therefore, the XPS/CA data for materials A, B, and D must be used with caution.

In light of the above data, we modified

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TABLE 1

XPS and CA Data on Zeolites

Material	Zeolite	Rhodium source	wt.% Rh	Rh_{3d}/Si_{2p}		XPS/CA	Si_{2p}/Al_{2p}		XPS/CA
				XPS	CA		XPS	CA	
A	RhCaA[a]	"Seed" RhNaA (3.76 wt.% Rh)	0.96	0.0201	0.0153	1.31	0.83	1.16	0.72
B	RhCaA[a]	$RhCl_3 \cdot xH_2O$	1.41	0.0869	0.0223	3.90	1.32	1.16	1.14
C	RhNaA[b]	Cation exchange of NaA with aqueous $RhCl_3$	1.25	1.33	0.022	60	0.90	1.00	0.90
D	RhCaA	Amorphous rhodium-aluminosilicate (8 wt.% Rh, Si/Al = 1)	1.20	0.0115	0.0202	0.57	1.18	1.07	1.10
E	RhCaA[d]	Precursor solution containing $[Rh(NH_3)_5Cl]Cl_2$	0.37	BDL[c]	0.0064	—	1.17	1.00	1.17
F	RhCaA[d]	$[Rh(NH_3)_5Cl]Cl_2$	0.33	BDL[c]	0.0053	—	1.14	1.00	1.14

[a] From (*1*).

[b] From (*5*).

[c] Below detection limits.

[d] RhNaA exchanged as described in (*1*).

our synthesis procedure in order to correct for the aforementioned shortcomings. First, instead of utilizing $RhCl_3 \cdot xH_2O$ which can be hydrolyzed by the basic zeolite A gel, we employed $[Rh(NH_3)_5Cl]^{2+}$ which remains intact under zeolite A synthesis conditions. (Rhodium–amine can be recovered from the filtrate of a synthesis solution.) Second, rather than adding a seed to the synthesis gel, we combined the rhodium–amine salt with a precursor solution of content similar to that observed for the solid phase early in the crystallization of pure zeolite A (*7*). Our premise was to allow the rhodium complex to interact with aluminum and silicon species prior to the fast crystallization which would occur upon addition of the remaining synthesis solution. Specifically, a precursor solution with composition $4.1Na_2O \cdot Al_2O_3 \cdot 3.1SiO_2 \cdot 100H_2O \cdot 0.07[Rh(NH_3)_5Cl]Cl_2$ was heated to 50°C for 1 h with high agitation. The remaining synthesis solution of composition $1.7Na_2O \cdot Al_2O_3 \cdot 0.2SiO_2 \cdot 172H_2O$ was added to the hot precursor solution and the temperature was elevated to 100°C. The total synthesis gel was of composition $3.0Na_2O \cdot Al_2O_3 \cdot 1.75SiO_2 \cdot 134H_2O \cdot 0.04 [Rh(NH_3)_5Cl]Cl_2$. Complete crystallinity was achieved in 4 h and the resulting material is denoted E. For comparison, rhodium–zeolite A was synthesized also by heating a gel of the above total composition for 4 h (material F). The synthesis of material F is similar to that of Kuehl (*8*), who synthesized rhodium–zeolite α in the presence of a rhodium pentaamine chloride salt.

Electron microprobe analyses of materials E and F showed them to be homogeneous in rhodium content. From infrared spectroscopy, it was ascertained that rhodium-amine complexes were present (appearance of amine stretching frequency) with the zeolite A. Also, no rhodium was detected in the superficial region by XPS. It is highly likely that some rhodium is present in the superficial area of the zeolite due to the fact that the XPS analysis should probe the top several unit cells. However, the rhodium content is probably below the detection limits of the spectrometer. Since the bulk chemical analysis shows the presence of rhodium, the rhodium–amine complexes must be intrazeolitic. After exchanging the as-synthesized rhodium-containing zeolite A with $CaCl_2$ (*1*), the materials labeled RhCaA in Table 1 were obtained. In these, the rhodium-amine complexes and the Ca^{2+} ions balance the negative charge of the zeolite A framework (no Na^+ is detected by XPS or by CA). Thus, the sum of the rhodium and calcium ions should equal half of the amount of aluminum in the solid. In the superficial region no rhodium is detected by XPS so the ratio Ca/Al should be 0.5. The Ca/Al ratio for materials E and F were 0.50 and 0.58, respectively. Material F must therefore contain occluded calcium. Thus, we believe that material E is slightly superior in purity to material F. Finally, since materials E and F were synthesized with high agitation, it is not surprising that the crystal sizes are submicron.

Zeolite A was also synthesized in the presence of $[Ru(NH_3)_5Cl]^{2+}$ in order to determine whether the procedure outlined above could be extended to the use of other transition metal amines. Ruthenium–zeolite A was successfully synthesized with this procedure by exactly repeating the technique outlined above except that $[Ru(NH_3)_5Cl]Cl_2$ was substituted for $[Rh(NH_3)_5Cl]Cl_2$. The RuCaA (RuNaA after $CaCl_2$ exchange) contained 0.9 wt% Ru. Electron microprobe analysis of this material showed that the ruthenium was nearly uniform in distribution from crystal to crystal although several areas of slightly higher ruthenium concentration were observed.

TABLE 2

CO-Hydrogenation Catalytic Behavior of RuCaA (T = 255°C, P = 2.3 atm, CO conversion = 8.5%, time on-stream = 104 min)

Product	Distribution of hydrocarbons	
	Mole (%)	Carbon (%)
Methane	70.2	45.6
Ethane/ethylene	11.0	14.3
Propylene	10.5	20.5
Propane	2.6	5.1
Butane	3.5	9.0
trans-2-Butene	0.3	0.8
cis-2-Butene	1.8	4.7

The RuCaA was tested for catalytic activity in a fixed-bed reactor. Approximately 1.5 g of RuCaA was contacted with flowing $CO:H_2$ (1 : 1) at 255°C and 2.3 atm. The gas flow rate was 10 ml(STP)/min. Prior to syngas exposure, the catalyst was reduced in H_2 at 275°C overnight. Table 2 shows the distribution of hydrocarbon products. Note that all the products are linear, that none larger than butane are formed, and that the distribution is non-Schultz–Flory. These data are representative of the catalytic behavior during the initial few hours on-stream. As the process time increased the CO conversion decreased and the hydrocarbon distribution shifted to the production of slightly higher molecular weight hydrocarbons. This change in hydrocarbon distribution probably is not due to the migration of ruthenium to the zeolite surface since no increase in ruthenium content is detected by XPS after reaction (*6*). Complete details of the CO-hydrogenation behavior of the RuCaA materials as well as full characterizations of the solid as-synthesized, *in situ* during catalysts, and after exposure to the reaction environment will be presented later (*9*).

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