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Propylene Hydroformylation on Rhodium Zeolites X and Y

I. Catalytic Activity

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Propylene hydroformylation activity at atmospheric pressure over RhNaX and RhNaY is a function of the cation-exchange procedure. The best method for the preparation of catalysts with reproducible activity is NaY exchange at pH 6 and 90°C by dropwise addition of aqueous $RhCl_3$ with subsequent stirring for 5 h. These catalysts show activity for hydrogenation, hydroformylation, and synthesis of C_7-ketones. Reaction selectivity is a function of the exchange conditions and activation procedure. The rate dependence upon the partial pressures of carbon monoxide, hydrogen, and propylene is similar to that reported for homogeneous hydroformylation. The selective poisoning of an active RhNaY catalyst is consistent with hydroformylation active sites located on the surface of the zeolite particles.

INTRODUCTION

The development of heterogeneous rhodium hydroformylation catalysts has been the goal of many investigations. Most of this work has been centered on the attachment of rhodium to polymeric supports (*1*, *2*), although the use of inorganic oxides and zeolites also have been studied (*3–7*). Several recent reviews in this area are available (*1, 2, 8*). The immobilization method of interest to this report is the incorporation of rhodium into zeolites by ion exchange.

The intrazeolite chemistry of rhodium has been developed primarily as a means of immobilizing a rhodium methanol carbonylation catalyst (*9–20*). Rhodium may be introduced via cation exchange of $RhCl_3$(aq) and $Rh(NH_3)_5Cl^{2+}$(aq), or by impregnation of $HRh(CO)(PPh_3)_3$ (Ph = phenyl). In the last case, the rhodium resides exclusively on the surface of the zeolite particles since the complex is too large to pass through the channels of even the large-pore faujasites. More recently, rhodium zeolites have been used as hydroformylation (*4–7*) and hydrogenation (*21*) catalysts. Other noncatalytic studies have concentrated on determining the location of rhodium within zeolites (*22–24*) and on the formation of rhodium carbonyl (*22, 24–27*) and rhodium carbonyl phosphine (*22*) complexes.

Very recently, the concept of coordination catalysis by intrazeolitic rhodium catalysts has been challenged. Denley *et al.* (*28*) suggest from EXAFS studies of rhodium-exchanged NaX that the active form of rhodium for the carbonylation of methanol is metallic rhodium particles. They also showed that rhodium oxide was formed with cation exchange using $RhCl_3$(aq), and that the oxide was incompletely converted to metal after exposure to the methanol carbonylation environment. However, Van't Blik *et al.* (*29*) using *in situ* EXAFS experiments showed that for rhodium oxide supported on γ-Al_2O_3 the adsorption of CO converted small rhodium crystallites into isolated $Rh(CO)_2$ species. If, in fact, rhodium is present as rhodium oxide on the RhNaX catalysts after cation exchange with $RhCl_3$(aq), then reduction by CO may still yield well-dispersed rhodium carbonyls. These results have important conse-

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quences for further investigations of rhodium zeolite catalysts. It is clear that *in situ* analyses are required for proper study.

It is interesting to note that cation exchange of $RhCl_3$(aq) with NaY did not appear to produce rhodium oxide (based upon comparisons to $Rh(H_2O)_6^{3+}$-exchanged NaY) (*24*). The exchange of rhodium into a variety of zeolites with different pore sizes showed that simultaneous cation exchange and slow hydrolysis of the aqueous rhodium species occurred. In large-pore zeolites, such as NaY, exchange predominated, while hydrolysis was overwhelming with the small-pore aluminosilicates.

The objective of this investigation was to continue our study of propylene hydroformylation with rhodium-exchanged NaX and NaY (*6*). We combined the results of catalytic activity and *in situ* FTIR experiments to further probe the catalytic and coordination chemistry of rhodium-exchanged zeolites. Part I is devoted to the study of catalytic activity. The zeolite type, the rhodium exchange cation, the ion-exchange conditions, the catalyst pretreatment, and the reaction environment were varied in order to determine their effects on the catalytic activity. Part II is devoted to the *in situ* FTIR studies of rhodium carbonyl formation and location, and in the identification and location of reaction intermediates.

EXPERIMENTAL

Materials. Rhodium trichloride trihydrate was obtained on loan from Johnson Matthey. The rhodium compounds $[Rh(NH_3)_5Cl]Cl_2$ (*30*) and $[Rh(NH_3)_5H_2O]Cl_3$ (*31*) were synthesized by literature methods. Zero-grade nitrogen and hydrogen were purchased from AIRCO, and carbon monoxide (99.5%) and propylene were obtained from Matheson Company. The zeolites used were Molecular Sieve 13X and 13Y purchased in powder form from Strem Chemical Company. The silica used was Davison 62 manufactured by W. R. Grace. Phosphines were purchased from Strem Chemical Company and were used without further purification.

Preparation of catalyst. The zeolite powder was washed with distilled H_2O and dried in air at 120°C for 24 h. The powder (2 g) was slurried in distilled water or a NaCl solution (100 ml) at 90°C. A 100-ml solution of $RhCl_3 \cdot 3H_2O$ was added dropwise over a 1-h period to the zeolite slurry. For most preparations the pH of the slurry was maintained at a specified level by addition of 0.1 *N* NaOH. When the addition of the rhodium solution was completed, the zeolite slurry was stirred for 0–24 h at 90°C, after which it was allowed to cool to room temperature. The zeolite was filtered, then dried in air at 120°C to a free flowing powder.

Cation exchange of $[Rh(NH_3)_5H_2O]^{3+}$ and $[Rh(NH_3)_5Cl]^{2+}$ for Na^+ in NaX and NaY was performed by dissolving the complex in water and adding to a water slurry of the zeolite. The temperature (50 or 95°C) was maintained overnight after which the zeolite was filtered and washed with water. The powder was then dried at room temperature.

Cation exchange of $[Rh(NH_3)_5H_2O]^{3+}$ with silica was performed by dissolving the complex in aqueous NH_4OH which contained slurried silica. The temperature was held constant at 80°C overnight after which the solid was filtered, washed, and dried at room temperature.

The rhodium content of the solid catalysts were determined by atomic absorption spectroscopy after digestion of the solid with acid.

For reaction runs, the rhodium-exchanged zeolite powder was compacted without binder into pellets which were subsequently crushed and size separated. The particles were −40/+70 mesh. Approximately 0.8 g of catalyst was loaded into the reactor.

Reactor system and procedure. The hydroformylation of propylene was carried out in a differential fixed-bed reactor system which has been described elsewhere

(*6*). For certain runs, a Hewlett–Packard gas chromatograph–mass spectrometer was placed on line to analyze the reactor effluent stream.

The reactor start-up was dependent upon the catalyst pretreatment. In this study four catalyst pretreatments were used. (i) A nitrogen pretreatment consisted of heating the catalyst bed to 120°C under flowing N_2 (50 cm^3(STP)/min), after which reactant gases were introduced and the temperature raised to 150°C. (ii) The catalyst was dried *in situ* by a stream of flowing dry air at 190°C for 5 h, and cooled to 150°C under N_2 (50 cm^3(STP)/min). The catalyst was then contacted with reaction gases. (iii) Precarbonylation of the reactor charge was accomplished by introducing CO into the reactor at 15–20 cm^3(STP)/min, then pressurizing to 3 atm. The catalyst was maintained at 120°C under flowing CO for 12 h. The reaction gases were then introduced and the temperature elevated to 150°C. (iv) Following the procedure of Takahashi and Kobayashi (*4*), the catalyst was heated to 127°C under a flowing mixture of N_2 and H_2 (10% H_2) and maintained at 127°C for 5 h, after which the reactant mixture was introduced and the temperature raised to 150°C.

The normal reaction conditions were a 3/3/2/1/ mixture of H_2/propylene/N_2/CO flowing at 45 cm^3(STP)/min at 150°C and atmospheric pressure.

RESULTS

The ability to initiate hydroformylation activity was directly dependent upon the cation-exchange conditions. Catalyst preparations giving hydroformylation products are listed in Table 1. The changes in activity with process time for catalysts A and E are illustrated in Figs. 1 and 2, respectively. Figure 1 is reproduced from (*6*) for ease in comparison to Fig. 2. During start-up, 2-propanol, 2-pentene, and several unidentified compounds are formed. With time, these components decrease in magnitude, and at steady state are not present in the product stream. As the system approaches steady state, five products that are formed other than propane and the two butyraldehydes are isobutanol, *n*-butanol, 2,4-dimethyl-3-pentanone, 2-methyl-3-hexanone, and 4-heptanone. At steady state, the 2,4-dimethyl-3-pentanone is not present in the

TABLE 1

Catalyst Preparations That Show Hydroformylation Activity[a]

Catalyst	Exchange pH	[NaCl] (*N*)	Zeolite	wt% Rh	Selectivity[b,c]	Regioselectivity[b,d]
A	6	0.1	NaY	3.4	3.4	1.9
B	6	0.1	NaY	2.0	4.7	1.9
C	6	0.1	NaY	1.0	5.5	1.6
D	8	0.1	NaY	4.0	3.7	2.0
E[e]	6	0.0	NaY	4.0	4.2	2.4
F[f]	6	0.2	NaY	4.0	—	—
G	6	0.1	NaX	2.7	11.7	2.0
Rh/SiO_2[g]	8	—	—	1.0	11.2	1.8

[a] Rhodium source: $RhCl_3 \cdot 3H_2O$, T = 90°C, time at T (°C) = 5 h.

[b] At 150°C, 1 atm.

[c] Hydrogenation/hydroformylation.

[d] *n*-Butyraldehyde/i-butyraldehyde.

[e] Required 56 h to reach steady state.

[f] Ketone products only.

[g] See text for preparation

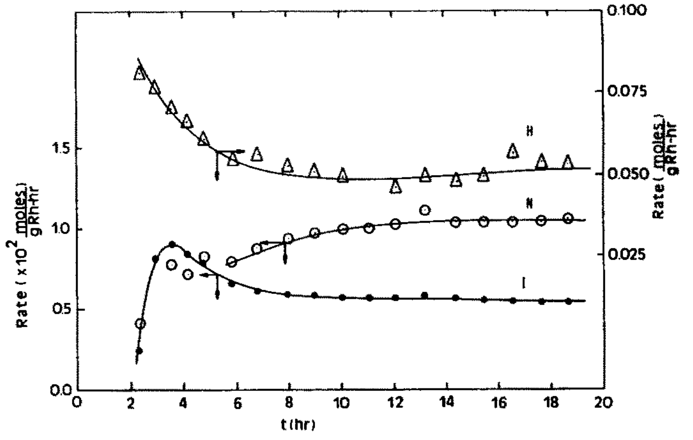


FIG. 1. Reaction rates versus process time for catalyst A. Reaction conditions: 150°C, 1 atm. H, Hydrogenation: N, *n*-butyraldehyde; I, isobutyraldehyde. Reproduced from (*6*).

reactor effluent stream and the total amount of the remaining four side-products (excluding propane) is less than 5% of the aldehydes produced. All catalyst preparations other than E and F behaved similarly to the data shown in Fig. 1 for catalyst A. Typically, propylene hydrogenation activity declines as hydroformylation activity increases, and the rate of isobutyraldehyde production goes through a maximum. Steady state is achieved in approximately 16 h. For catalyst E (Fig. 2), approximately 56 h are required to reach steady state. Also, notice that hydrogenation increases over the start-up period as does the production of aldehydes. Catalyst F hydrogenated propylene to propane and produced 2-methyl-3-hexanone and 4-heptanone in a 1 : 2 ratio at steady state. No other products were present in the reactor effluent stream. Finally, NaY which was slurried in NaCl at 90°C did produce 2-methyl-3-hexanone and 4-heptanone at 150°C from a reaction mixture of propylene, H_2, CO, isobutyraldehyde, and *n*-butyraldehyde.

Table 2 summarizes the reactivity data for catalyst A with the complete series of pretreatments. The only significant varia-

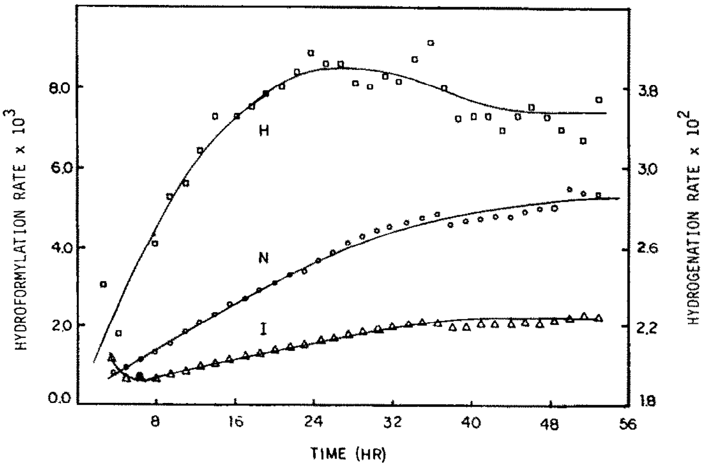


FIG. 2. Reaction rates versus process time for catalyst E. Reaction conditions: 150°C, 1 atm. H, Hydrogenation; N, *n*-butyraldehyde; I, isobutyraldehyde.

TABLE 2

Effect of Pretreatment on Catalytic Activity, Catalyst A at 150°C, 1 atm

	Pretreatment			
	Carbonylation	Air	N_2	H_2/N_2
C_3H_8, Rate $\left(\frac{\text{mol}}{\text{g Rh} - \text{h}}\right)$	4.5×10^{-2}	1.94×10^{-2}	2.66×10^{-2}	0.66×10^{-2}
n-C_4H_8O, Rate $\left(\frac{\text{mol}}{\text{g Rh} - \text{h}}\right)$	8.3×10^{-3}	2.04×10^{-3}	8.67×10^{-3}	0.37×10^{-3}
i-C_4H_8O, Rate $\left(\frac{\text{mol}}{\text{g Rh} - \text{h}}\right)$	4.8×10^{-3}	1.11×10^{-3}	3.91×10^{-3}	0.27×10^{-3}
i-C_4H_8O, E^a (kcal/mol)	—	12.1	14.9	—
n-C_4H_8O, E^a (kcal/mol)	—	10.3	13.7	—
Regioselectivity	1.73	1.84	2.21	1.37
Selectivity	3.44	6.16	2.11	10.2

[a] At 120–150°C.

tions in activity with pretreatment occur for the H_2/N_2 exposure. In this case, the rates are significantly lower, the selectivity is poorer, and the regioselectivity is lower than for other pretreatments. Interestingly, hydroformylation activation is possible at 127°C with pretreatment (iv), while for all other pretreatments, 150°C is required to initiate activity.

Figure 3 shows a representative plot of the temperature effects on reaction rates. In all cases, the activation energy plots show no curvature.

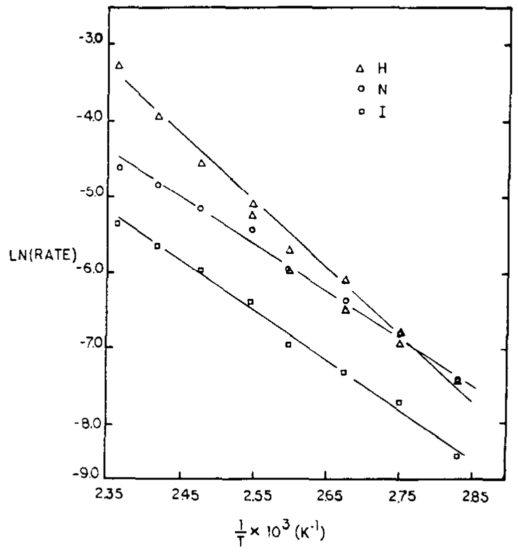


FIG. 3. Effects of temperature on reaction rates for catalyst A. H, Hydrogenation; N, n-butyraldehyde; I, isobutyraldehyde.

The effects of component partial pressures were correlated in terms of power-law kinetic models and the results are given in Table 3. A nonlinear least-squares algorithm was used to obtain the parameter estimates shown.

The location of the active sites on catalyst A was performed as follows. Steady state at 150°C and 1 atm was achieved after which hexyldiphenylphosphine (HDP) was injected into the flowing reactant stream. Three stoichiometric equivalents to the to-

TABLE 3

Kinetic Parameters for Hydroformylation and Hydrogenation at $T = 150°C$ and 1 atm Total Pressure

$$\text{Rate} \left(\frac{\text{mole}}{\text{g Rh} - \text{h}}\right) = A \exp[-E/RT] P^{\alpha}_{C_3^=} P^{\beta}_{H_2} P^{\gamma}_{CO}$$

	C_3H_8	i-C_4H_8O	n-C_4H_8O
A	4.12×10^6	1.36×10^3	1.86×10^3
E^a (kcal/mol)	15.8	11.0	10.8
α	1.01	1.00	0.97
β	0.35	0.40	0.48
γ	−0.71	−0.70	−0.72

[a] At 120–150°C.

TABLE 4

Catalyst Preparations that Show No Hydroformylation Activity

Rhodium source	Exchange pH	T (°C)	Time (h)	[NaCl] (N)	Zeolite	wt% Rh
$RhCl_3 \cdot 3H_2O$	6	90	24	0.1	NaY, NaX	1–4
$RhCl_3 \cdot 3H_2O$	6	90	0[a]	0.1	NaY	4
$RhCl_3 \cdot 3H_2O$	4	90	5	0.1	NaY	4
$RhCl_3 \cdot 3H_2O$	4	90	5	0	NaX, NaY	4
$[Rh(NH_3)_5Cl]Cl_2$	8	50	12	—	NaY, NaX	1–4
$[Rh(NH_3)_5H_2O]Cl_3$	8	50	12	—	NaY	1
$[Rh(NH_3)_5H_2O]Cl_3$	8	95	12	—	NaY	1

[a] Slurry cooled to 5°C immediately following the addition of $RhCl_3 \cdot 3H_2O$.

tal amount of rhodium in the reactor were added. The steady-state behavior of the catalyst was altered by the presence of HDP.

Preparations that failed to exhibit hydroformylation activity are listed in Table 4. All catalyst preparations showed hydrogenation activity which decreased with time to a steady-state value. The catalyst prepared by aqueous $RhCl_3$ exchange at pH 4 in the absence of NaCl did not produce butyraldehydes but instead a spectrum of 10 compounds which were not identified. Blank NaY which was slurried in distilled water did not convert any of the reactants at 150°C and 1 atm. However, NaY which was slurried at pH 4 gave the same distribution of 10 products as mentioned above. Interestingly, the rhodium catalyst exchanged at pH 4 could be activated by H_2/N_2 pretreatment to give at steady state 4-heptanone and 2-methyl-3-hexanone in a 2 : 1 ratio as well as *n*- and isobutyraldehyde in a 1.2 : 1 ratio. The aldehyde production rates were similar to those shown in the second column of Table 2 and the ratio of ketones to aldehydes was approximately 5 : 1.

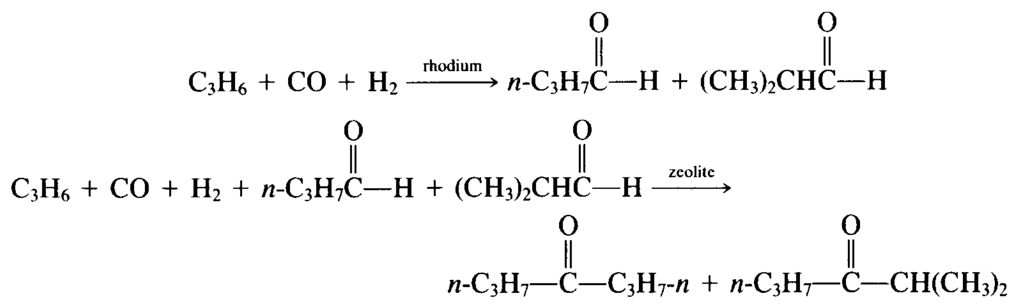
DISCUSSION

The RhNaX and RhNaY catalysts are active for hydrogenation and hydroformylation of propylene at atmospheric pressure. However, the procedure for preparing active material is quite specific and will be discussed in detail below. Hydroformylation activity is initiated for all catalyst pretreatments other than H_2/N_2 when the catalysts are contacted with reactant at 150°C. This temperature is also required to activate Rh/SiO_2. Once activated, these catalysts show hydroformylation activity at temperatures as low as 80°C (see Fig. 3). As previously discussed (*6*), we do not believe the activation process involves the reduction of rhodium as postulated by Scurrell and Howe (*13*) for methanol carbonylation, but rather the formation of an active species involving a rhodium hydride. Indirect evidence of hydride formation is presented in the following paper (*32*). Originally, we proposed that the rhodium species active for hydrogenation converted into hydroformylation active species. This was due to the fact that hydrogenation decreased as hydroformylation increased and both reactions reached steady state simultaneously (*6*). Since catalysts that show no hydroformylation activity give similar hydrogenation start-up profiles as those catalysts with hydroformylation activity, the decline in the rate of hydrogenation must not be due to the loss of hydrogenation species by conversion into active hydroformylation sites.

The isobutyraldehyde rate goes through a maximum for most catalyst preparations. The decrease in isobutyraldehyde production could be attributed to a loss of rhodium during the activation process. A similar behavior for isobutyraldehyde production with cobalt-exchanged zeolites has been observed and was postulated to occur from the loss of cobalt (*33*). Also, Arai *et al.* (*34*) noticed that $Rh_2Cl_2(CO)_4$ was formed and sublimed from $RhCl_3$ on silica gel at conditions similar to ours. Additional indirect evidence for rhodium loss is provided by the fact that carbonyl stretching bands observed in the infrared spectrum were sharper on the spent catalysts than on the precarbonylated catalysts (*35*). It is possible that the rhodium loss occurred only during activation since steady state could be maintained for approximately 1 week. Also, Takahashi and Kobayashi (*4*) reported constant activity for over 1 month. Atomic absorption analysis of the catalysts before and after reaction did not indicate a difference in rhodium content within experimental error. We believe that our rhodium detection procedure does not possess the sensitivity required to notice slight changes in rhodium content (experimental error is approximately ±0.1 wt% Rh).

During start-up, 2-propanol, 2-pentene, and several other unidentified compounds were formed. We postulate that propionaldehyde is produced from propylene and the water contained within the zeolite via a Wacker-type mechanism (*36*). This accounts for C_3 containing alcohols. Furthermore, Takahashi *et al.* (*37*) have shown that propionaldehyde can desorb from RhNaY to produce propanol and pentene. The hydrogenation of propionaldehyde and the unknown steps to produce pentene must be fast on our preparations because no propionaldehyde was observed in the reactor effluent stream. A partial characterization of the unidentified products formed during start-up can be found elsewhere (*35*). None of these compounds are present at steady state.

As the catalysts approach steady state isobutanol, *n*-butanol, 2,4-dimethyl-3-pentanone, 2-methyl-3-hexanone, and 4-heptanone are produced, but form at less than 5% of the isobutyraldehyde and *n*-butyraldehyde production. At steady state, no 2,4-dimethyl-3-pentanone was observed. Obviously, *n*- and isobutyraldehyde were being hydrogenated to their associated alcohols. Since NaY was not able to produce aldehydes from propylene/H_2/CO but was capable of producing ketones from a reactant stream consisting of propylene/H_2/CO/aldehydes, we propose that the following reactions occur at steady state on RhNaY catalysts to yield ketones (*38*):



$$C_3H_6 + CO + H_2 \xrightarrow{\text{rhodium}} n\text{-}C_3H_7\overset{\overset{O}{\|}}{C}\text{—}H + (CH_3)_2CH\overset{\overset{O}{\|}}{C}\text{—}H \qquad (1)$$

$$C_3H_6 + CO + H_2 + n\text{-}C_3H_7\overset{\overset{O}{\|}}{C}\text{—}H + (CH_3)_2CH\overset{\overset{O}{\|}}{C}\text{—}H \xrightarrow{\text{zeolite}}$$
$$n\text{-}C_3H_7\text{—}\overset{\overset{O}{\|}}{C}\text{—}C_3H_7\text{-}n + n\text{-}C_3H_7\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH(CH_3)_2 \qquad (2)$$

Equations (1) and (2) outline a bifunctional synthesis of ketones. The second step may occur at acid sites in the zeolite.

We have not observed aldol condensation products from any catalyst included in this study. We also have evidence from *in situ* infrared spectroscopy that aldol condensation products were not present on the zeolite during reaction (*32*). It is interesting that we do not observe aldol condensation reactions since Gerritsen *et al.* (*39*) showed that at 90°C aldol condensation occurs with supported liquid-phase catalysts. At reaction conditions the zeolite is probably acidic. Acid-catalyzed aldol condensation proceeds through the enol form of the aldehyde. Thus, one possible explanation for our selectivity is that enolization is not occurring on the zeolite.

Catalysts E and F produced start-up behavior different from that described above. With catalyst E, hydrogenation increased with process time and approximately 56 h were required to reach steady state. Catalyst F showed the typical decline in hydrogenation activity but the only other products were 2-methyl-3-hexanone and 4-heptanone produced in a 1 : 2 ratio.

The data provided in Tables 1 and 4 show that the procedure for preparing an active catalyst was quite specific. No hydroformylation activity was observed from any preparation where the rhodium was introduced as an ammine complex. Primet *et al.* (*25*) reported that exposure to O_2 at 350°C removed the NH_3 ligands from rhodium ammine complexes exchanged with zeolites. Scurrell and Howe (*13*) claimed to be able to perform NH_3 removal by N_2 at 400°C. We exposed our ammine preparations to the following conditions: (i) air at 400°C, (ii) O_2 at 400°C, (iii) air at 250°C, and (iv) CO at 120°C. None of these treatments yielded an active catalyst. However, we did observe a very interesting result using the ammine preparations. If 1.0 ml of H_2O was injected into the reactant stream, the catalyst bed immediately exothermed 20°C. A sample taken 5 min after the injection showed the presence of propionaldehyde, isobutyraldehyde, and *n*-butyraldehyde in quantities far exceeding those obtained at steady state from the active catalysts. Unfortunately, the activity quickly declined to zero. A second injection of H_2O again promoted activity, but subsequent injections did not. Continuous exposure to a reactant stream containing trace amounts of H_2O failed to promote activity other than the initial burst similar to that observed from a single injection of H_2O. It is unknown to us why the ammine preparations do not activate at atmospheric pressure. These materials are known to be active for methanol carbonylation at atmospheric pressure (*9, 10*) and liquid-phase hydroformylation at 20 atm (*7, 40*).

The exchange of aqueous $RhCl_3$ at a pH of 6 or above with NaY and NaX produced active catalysts. With RhNaX, we could not consistently reproduce the reaction rates shown in Table 1 for catalyst G. On the other hand, the NaY-supported rhodium catalysts were always reproducible. The catalyst preparations exchanged at pH 4 did not show hydroformylation activity, but rather activity toward a broad spectrum of products. Since blank NaY which was slurried at pH 4 gave the same product distribution, the observed catalysis did not involve rhodium and probably was due to acid sites on the zeolite. Upon completion of the dropwise addition of the aqueous $RhCl_3$, the zeolite slurry was stirred for 0–24 h at 90°C. Interestingly, if the slurry was immediately quenched after rhodium addition or if it was allowed to stir at 90°C for 24 h, the resulting catalyst was inactive. Only those preparations that were stirred for 5 h showed hydroformylation activity.

Shannon *et al.* (*24*) have shown that for the exchange of aqueous $RhCl_3$ with NaY at 90°C and at a pH 4 the exchanging cation is trivalent. As the pH of the zeolite slurry is increased, other rhodium species such as $[Rh(H_2O)_{6-m}(OH)_m]^{3-m}$ may be present and could exchange into the zeolite. Also, once the rhodium species exchanges onto the zeolite subsequent hydrolysis can occur. Denley *et al.* (*28*) showed that rhodium oxide was formed in RhNaX by cation exchange of aqueous $RhCl_3$ with NaX. We postulate that during the stirring of the rhodium-exchanged zeolite at pH 6 hydrolysis is occurring and that if left long enough (24 h), the rhodium will ultimately end up as rhodium oxide. Shannon *et al.* (*24*) report rhodium oxide on the surface of NaA. We fail to activate RhNaA for hydroformylation. Thus, it is plausable that the formation of rhodium oxide by allowing the zeolite slurry to stir for 24 h is the cause of inactivity on RhNaY. It is not clear why the rhodium species present on the zeolite from exchange at (i) pH 4 and (ii) pH 6 with immediate filtering after the dropwise addition of rhodium fail to produce active sites for hydroformylation.

The role of NaCl in the zeolite slurry is unclear, but it is obvious that it affects the ultimate catalytic activity. The absence of NaCl in the slurry alters the time the catalyst requires to reach steady state and the manner in which hydrogenation activity reaches steady state as shown in Fig. 2. The addition of 0.2 *N* NaCl completely changes the reaction selectivity by promoting the production of ketones. We believe that the role of the NaCl is probably that of changing the distribution of rhodium and proton among the various exchangeable sites within the zeolite.

The concentration of rhodium within the zeolite does not significantly alter the reactivity (catalysts A–C). The selectivity remains between 3 and 6 although there is a slight increase in regioselectivity with increasing rhodium content. The reaction rates for these catalysts are similar, and the rates for catalyst A are given in Table 2.

The effect of pretreatment on catalytic activity for catalyst A is shown in Table 2. There is little effect of pretreatment on catalytic activity for all treatments other than H_2/N_2. The values listed for the H_2/N_2 pretreatment in Table 2 agree well with those reported by Takahashi and Kobayashi (*4*). Thus, it appears that the ultimate behavior of the catalyst is determined once it has been dried. Exposure to 10% H_2 in N_2 decreases the activity of catalyst A as well as shifting the selectivity toward hydrogenation and the regioselectivity toward that observed in solution for binary rhodium carbonyls. The regioselectivity of our active materials is nearly 2 in all cases except for H_2/N_2 pretreatment. These values are approximately double that observed in solution for binary rhodium carbonyls (*41*). A regioselectivity of 1.8 is observed for Rh/SiO_2. Thus, the zeolite does not appear to show any shape selectivity; the increase in regioselectivity over that in solution is probably due to interactions of the rhodium active species with the support. The exposure to 10% H_2 in N_2 most likely reduces some of the rhodium to form aggregates on the surface of the zeolite. The hydroformylation active site could then form on these aggregates with minimal interaction with the zeolite. Thus, it is plausable that for the H_2/N_2 pretreatment the regioselectivity could differ from that of the other pretreatments. This also explains the drop in reaction rate by a lower dispersion of rhodium. Because of the reducing atmosphere, more rhodium metal would be present and could shift the hydrogenation activity to higher values. Complete reduction to rhodium metal must not occur with this pretreatment because we have previously shown (*6*) that rhodium metal on NaY does not hydroformylate propylene under these conditions. Another indication that the active site formed from H_2/N_2 pretreatment is different than that obtained from the other pretreatments is that H_2/N_2 exposure reduces the temperature required to initiate activity.

It is interesting to note that the catalyst prepared by $RhCl_3$(aq) exchange at pH 4 in the absence of NaCl which did not activate by air or carbonylation pretreatments did activate for hydroformylation after exposure to H_2/N_2. The regioselectivity of this catalyst was similar to catalyst A pretreated in the same manner but large amounts of ketones were produced. Once this catalyst has been activated for hydroformylation, we feel that ketone synthesis is most likely due to the high concentration of acid sites (exchanged at low pH). Recall that we postulated that ketone synthesis on catalysts A and F occurs at acid sites. However, the low-pH exchange catalyst does not require NaCl in the exchange slurry to create ketone synthesis sites.

The effects of component partial pressures, correlated in terms of power-law kinetic models, are given in Table 3. There is a first-order dependence upon propylene, an inhibition by carbon monoxide, and an approximate half-order dependence upon hydrogen for hydrogenation and hydroformylation. In general, a positive rate dependence upon olefin and hydrogen and inhibition by carbon monoxide have been observed in homogeneous hydroformylations with rhodium (*41*). Also, Arai (*42*) found similar partial pressure dependencies for the hydroformylation of propylene using rhodium bound to polystyrene-coated silica. These results in combination with *in situ* infrared studies (*32*) lead us to believe that propylene hydroformylation by rhodium–zeolite proceeds by a mechanism similar to that in solution by binary rhodium carbonyls. Thus, in contrast to the conclusion of Denley *et al.* (*28*) that methanol carbonylation occurs at heterogeneous rhodium sites, we feel that the catalytic activity for hydroformylation does arise from homogeneous-like catalytic sites fixed on the zeolite framework.

In an attempt to locate the active sites on catalyst A hexyldiphenylphosphine (HDP) was injected over the active catalyst. After 3 h, the isobutyraldehyde production was below our detection limit while the *n*-butyraldehyde and *n*-butanol rates were approximately half of their value prior to the HDP injection. Also, the production of 4-heptanone and 2-methyl-3-hexanone had tripled. The catalyst slowly deactivated and was completely unreactive 10 h after the HDP injection. Since HDP is too large to penetrate the faujasite, the active sites at steady state appear to be located on the surface of the zeolite crystals. An alternative explanation could be that HDP blocks the zeolite pores thus diminishing access to intrazeolitic active sites. The latter hypothesis is unlikely since it cannot account for the shifts in reaction selectivity.

Figure 3 illustrates the temperature dependence of the rates. These graphs show no curvature over the temperature range of 80 to 150°C. The absence of curvature in these figures suggests that mass transfer is not controlling the reaction rates (*43*). This result is much easier to rationalize if we postulate that the catalysis is occurring on the surface of the zeolite crystals. Finally, notice that as the temperature decreases so does the selectivity. At approximately 100°C the selectivity is one.

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