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Hydroformylation by Rhodium Zeolite A Catalysts

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A direct comparison of rhodium zeolite A catalysts for vapor- and liquid-phase 1-hexene hydroformylation is reported. Rhodium zeolite A catalysts prepared by ion exchange (surface rhodium) and by the synthesis procedure of Rossin and Davis (*J. Chem. Soc. Chem. Commun.* **234,** 1986) (intrazeolitic rhodium) hydroformylate 1-hexene in the vapor phase at 150°C and 2 atm total pressure and in the liquid phase at 20 atm and 50–120°C. Similar vapor-phase hydroformylation activity is obtained from the two preparations and both show rhodium loss after exposure to the reaction environment. The liquid-phase activity is somewhat different on these catalysts. The exchanged rhodium zeolite A elutes rhodium into the reaction mixture and the observed catalysis occurs via solution rhodium. The synthesized rhodium zeolite A does not elute rhodium as significantly as the exchanged catalyst. In the presence of cyclohexylmercaptan, a poison for solution and zeolite surface rhodium, the synthesized rhodium zeolite A catalyst reacted 1-hexene exclusively to heptanal at 120°C and 20 atm (H_2 : CO 1 : 1).

INTRODUCTION

Immobilized transition metals have been studied as hydroformylation catalysts in vapor- and liquid-phase conversions (*1–9*). These transition metal species have been supported on organic polymers (*1–3*), and inorganic materials such as carbon, alumina, silica, metal oxides (*2*), and zeolites (*2, 4–9*). To date, a major problem associated with polymeric supports is the serious loss of metal into the reaction mixture during liquid-phase operations (*1, 3, 10*). Metal loss also occurs into the liquid phase with inorganic supports and zeolites (*8, 9*), and has been shown to be not limited to liquid-phase operation. Cobalt carbonyls (*4*) and $Rh_2Cl_2(CO)_4$ (*11*) formed *in situ* during vapor-phase propylene hydroformylations were postulated to sublime from cobalt-exchanged zeolites and $RhCl_3$ impregnated silica gel, respectively. Thus, an immobilized transition metal catalyst which is able to perform liquid- and vapor-phase conversions without metal loss is presently not available.

The advantage of immobilizing transition metals within the pore structure of zeolites is the possible enhancements in reaction selectivity due to the molecular sieving effects of the zeolite. For the hydroformylation of α-olefins, reaction selectivity should be toward the production of linear aldehydes. Thus, if linear olefins could be hydroformylated within zeolite pore structures, the molecular discrimination performed by the zeolite must be between a linear and a branched aldehyde. Ideally, linear olefins would diffuse into the zeolite and produce only linear aldehydes due to the physical constraints imposed by the zeolite lattice. Zeolite CaA (calcium A) could be particularly beneficial in performing this discrimination since the pore size is approximately 5 Å. Linear hydrocarbons have been selectively hydrogenated in the presence of branched hydrocarbons by transition metal containing CaA (*12, 13*).

Rhodium is the preferred transition metal for hydroformylation due to its high activity and selectivity towards aldehyde produc-

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tion (*14*). Unfortunately, ion exchange of rhodium with zeolite A locates rhodium on the surface of the zeolite particles since cationic rhodium is too large to penetrate the 5 Å pores (*15*). Kuehl (*16*) circumvented the cation size problem by cocrystallizing rhodium with zeolite alpha (high silica containing type-A zeolite). His procedure consists of adding a rhodium salt to the zeolite synthesis gel in a manner similar that of Weisz *et al.* (*12*). Recently, Rossin and Davis (*17*) developed a new technique for producing intrazeolite transition metals with zeolite A. Basically, the procedure involved the addition of transition metal exchanged zeolite A "seed" crystals to the synthesis gel of zeolite A. The resulting product crystals contained intracrystalline transition metal.

The purpose of this investigation was to study hydroformylation by rhodium zeolite A catalysts in the vapor and liquid phases. The behavior of cation-exchanged RhCaA was compared to RhCaA synthesized by the technique of Rossin and Davis (*17*).

EXPERIMENTAL

Materials. Rhodium trichloride trihydrate was obtained on loan from Johnson Matthey Inc. $Rh_6(CO)_{16}$ was purchased from Strem Chemical Company. Zero-grade nitrogen and hydrogen and a 50–50 mixture of carbon monoxide and hydrogen were obtained from AIRCO, and carbon monoxide (99.5%) and a premixed (3 : 1) hydrogen–carbon monoxide cylinder were purchased from Matheson Company. Toluene, methanol, 1-hexene, 4-methyl-1-pentene, cyclohexene, and cyclohexylmercaptan were purchased from Aldrich Chemical Company.

Preparation of catalysts. $HRh(CO)(PPh_3)_3$ (Ph = phenyl) was synthesized by the procedure of Ahmed *et al.* (*18*). Zeolite NaA was synthesized by literature procedures, and the details are given elsewhere (*17*). The NaA crystals were cation-exchanged with $CaCl_2$ to give CaA.

Cation exchange of Rh^{3+} (from aqueous $RhCl_3$) for Ca^{2+} in CaA was performed as follows. The zeolite was slurried in 0.1 *N* $CaCl_2$ at 95°C. Then, an aqueous solution of $RhCl_3$ was added dropwise over a period of 1 h. The pH was maintained at 6.0 throughout the exchange by addition of saturated $Ca(OH)_2$ solution. The slurry was stirred at 95°C for 5 h and cooled with agitation overnight. The zeolite was filtered, washed with 2 liters of distilled water, and dried to a free flowing powder in flowing air at 120°C.

The RhCaA prepared by the procedure of Rossin and Davis will be denoted as synthesized RhCaA throughout the remainder of this report. The synthesis technique produces RhNaA which contains intracrystalline rhodium. The RhNaA crystals are exchanged with $CaCl_2$ or KCl to remove surface rhodium and to convert the RhNaA to RhCaA or RhKA, respectively. Complete details of the synthesis and supporting characterizations of the product crystals are given elsewhere (*19*).

Atomic absorption spectroscopy was used to obtain chemical analysis (CA) of the solids after acid digestion. XPS (X-ray photoelectron spectroscopy) spectra were obtained on the solids using a Kratos XSAM 800 spectrometer with Mg$K\alpha$ X-rays. Superficial to bulk element contents were evaluated using element ratios determined from XPS and CA.

For vapor-phase reaction runs, the RhCaA powders were compacted without binder into pellets which were subsequently crushed and size-separated. The particles were −40/+70 mesh. Approximately 0.7–1.5 g of catalyst were loaded into the reactor.

Reactor systems. Liquid-phase hydroformylations were performed in a 600-ml Parr autoclave. A constant head pressure was maintained by the premixed cylinders (1 : 1 or 3 : 1 $H_2 : CO$), while constant agitation assured good mixing. The temperature was controlled to ±1°C by the heating mantle-temperature controller supplied with the autoclave. The rhodium content of the liquid filtered from the reactor was determined spectrophotometrically by the procedure of Lang *et al.* (*10*).

Vapor-phase hydroformylations were carried out in a differential fixed-bed reactor at 2 atm total pressure. The reactor itself was a stainless-steel tube buried in a fluidized bed heat exchanger. A thermocouple immersed in the catalyst bed was used to monitor the reactor temperature, which was maintained at ±1°C. Carbon monoxide, hydrogen, and nitrogen were fed through separate rotameters and scrubbed to remove trace oxygen, water, and hydrocarbons. These gases were mixed, heated, and contacted with the olefin in a vaporizer. The olefin was fed to the vaporizer via a syringe pump. The normal reaction mixture was 3/1/2/1 H_2/olefin/N_2/CO flowing at 35 cm^3 (STP)/min. The product stream was analyzed by an on-line Hewlett–Packard GC–MS. Complete details of this system are available (*20*).

The cyclohexylmercaptan was introduced into the heated reactant stream by syringe injection of approximately 1 cm^3 in size.

Vapor-phase hydroformylation procedure. Three catalyst pretreatment/start-up sequences were performed. (i) Precarbonylation of the reactor charge was accomplished by introducing CO into the reactor at 20–30 cm^3 (STP)/min, then pressurizing to 3 atm. The catalyst was maintained at 120°C under flowing CO for 12 h. Next, the reactor temperature was raised to 150°C while simultaneously reducing the pressure to 2 atm and introducing the reactant mixture. (ii) The catalyst was contacted with flowing dry air at atmospheric pressure while the temperature was quickly increased from ambient to 150°C. Once the reactor reached 150°C, reactants were introduced and the pressure was increased to 2 atm. (iii) Following the procedure of Takahashi and Kobayashi (*6*), 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.

RESULTS

Liquid-phase hydroformylation. The results obtained from 1-hexene hydroformylation at 20 atm H_2 : CO at 1 : 1 and 3 : 1 and 50°C in 1 M 1-hexene in toluene by rhodium zeolite A catalysts are given in Table 1. For these experiments and all others reported in this section, no hydrogenation to hexane or seven carbon alcohols, and no aldol condensation products are observed. The X-ray diffraction pattern of the catalysts prior to and after hydroformylation

TABLE 1

Liquid-Phase Hydroformylation of 1-Hexene by Rhodium Zeolite A

Catalyst	H_2/CO	Rh. conc. mmol/liter	Conversion[c]	Selectivity[d]	n/b[e]	Aldehyde distribution (mol%)		
						Heptanal	2-Methylhexanal	2-Ethylpentanal
RhNaA (0.08% Rh)[a]	1	0.025	0.004	—	—	—	—	—
RhCaA (0.08% Rh)[a]	1	0.025	0.213	0.264	2.73	4.1	1.5	—
RhCaA (0.07% Rh)[a]	3	0.041	0.960	0.310	2.36	20.9	8.9	—
RhKA (0.07% Rh)[a]	3	0.035	0.020	—	—	—	—	—
RhCaA (2% Rh)[b]	1	0.646	1.000	0.960	0.76	41.5	42.0	12.7

Note. 20 atm, 50°C; 1 *M* 1-hexene in toluene; run time = 22 h.

[a] Synthesized rhodium zeolite A.

[b] Cation-exchanged rhodium zeolite A. From (*9*).

[c] Fraction of 1-hexene consumed.

[d] Aldehydes produced/1-hexene consumed (2- and 3-hexene side products).

[e] Ratio of normal to branched aldehydes.

are the same indicating no loss in crystallinity during reaction. No rhodium is detected in the liquids contacted with the synthesized rhodium zeolite A catalysts while most of the rhodium initially present on the exchanged RhCaA is found in the reaction fluid at the completion of the run.

A synthesized RhCaA (0.96% Rh) catalyst produced 26% conversion of 1-hexene (1 *M* in toluene) at 50°C, 20 atm (1 : 1 H_2 : CO) in 22 h of contact (total rhodium concentration of 0.1 mmol/liter). The solution recovered from this reaction contained 0.01 mmol/liter of rhodium.

Mercaptans are known to poison rhodium catalysts (*21*). Cyclohexylmercaptan is used as a poison in this study since the cyclohexyl group does not allow the mercaptan to penetrate the zeolite pore system. Thus, this mercaptan will only poison solution and zeolite surface rhodium. When the 0.96% Rh RhCaA catalyst is contacted with 1-hexene under the conditions listed in the previous paragraph with the addition of cyclohexylmercaptan, no reaction is observed. A similar result is obtained with $Rh_6(CO)_{16}$. When the temperature is raised to 120°C and the concentration of 1-hexene lowered to 0.1 *M* with all other conditions remaining the same as above, 1.5% conversion of 1-hexene is produced from RhCaA (0.96% Rh). Interestingly, only one product is formed; heptanal. Once solution and surface rhodium are poisoned, the RhCaA catalyst is 100% selective to the linear aldehyde. This catalyst was filtered from the reaction fluid and used in three additional batch experiments. Each experiment showed similar conversion and selectivity. The rhodium content of this catalyst after each batch is shown in Fig. 1.

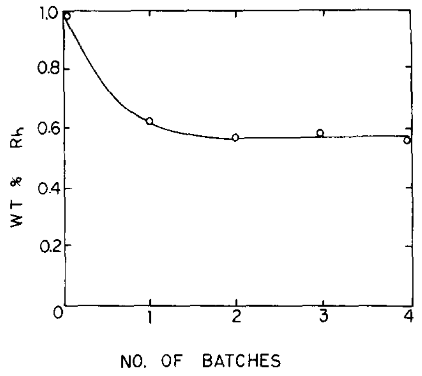


FIG. 1. Weight percentage rhodium in RhCaA (synthesized) after exposure to several batch reactions. Batch conditions: 0.1 *M* 1-hexene in toluene, 20 atm (1 : 1 H_2 : CO), 120°C, 22 h contact, addition of cyclohexylmercaptan.

The effects of solvent type on homogeneous and heterogeneous 1-hexene hydroformylation at 20 atm H_2 : CO (1 : 1) and 50°C are shown in Table 2.

TABLE 2

Effect of Solvent on Hydroformylation

Catalyst	Run time (h)	Rh conc. (mmol/liter)	Solvent	Conversion	Selectivity	n/b	Aldehyde distribution (mol%)		
							Heptanal	2-Methylhexanal	2-Ethylpentanal
$Rh_6(CO)_{16}$	3.25	0.573	Toluene	0.99	0.377	1.66	23.2	12.6	1.4
$Rh_6(CO)_{16}$	3.25	0.573	Methanol	0	—	—	—	—	—
$Rh_6(CO)_{16}$	22.5	0.607	Toluene	1.00	0.973	0.80	43.6	41.4	12.3
$HRh(CO)(PPh_3)_3$ + 20 PPh_3[a]	22.0	0.45	Toluene	1.00	1.000	2.77	73.4	26.8	—
$HRh(CO)(PPh_3)_3$ + 20 PPh_3[b]	22.0	0.45	Methanol	1.00	1.000	3.06	75.3	24.3	0.4
Rh–silica (1.4% Rh)[a]	22.0	0.630	Toluene	1.00	0.753	1.01	37.9	30.1	7.3
Rh–silica (1.4% Rh)[b]	22.0	0.685	Methanol	0.02	—	—	—	—	—
RhCaA (0.08% Rh)[c]	22.0	0.025	Toluene	0.21	0.264	2.73	4.1	1.5	—
RhCaA (0.08% Rh)[c]	22.0	0.025	Methanol	0.19	0.193	2.04	2.4	1.2	—

Note. 20 atm, 50°C; 1 *M* 1-hexene in solvent.

[a] From (*9*).

[b] Same catalyst as used in (*9*).

[c] Synthesized rhodium zeolite A.

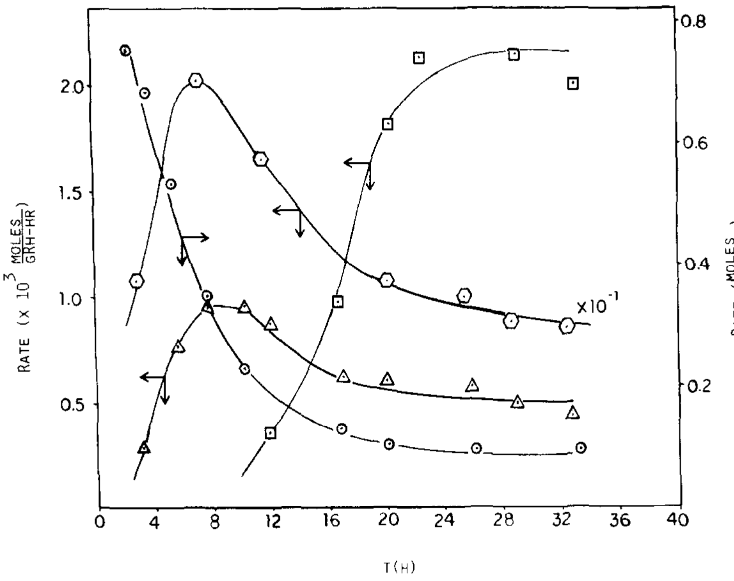


FIG. 2. Reaction rates versus time for RhCaA (synthesized). Catalyst was precarbonylated. ○, Hexene isomers; △, 2-methylhexanal; □, heptanal; ⬡, hexane.

Vapor-phase hydroformylation. Figure 2 shows the changes in activity with process time when a synthesized RhCaA catalyst is precarbonylated and exposed to 1-hexene hydroformylation conditions. The process time is shown to begin when the catalyst bed reached 150°C. Initially, isomerization, hydrogenation, and trace hydroformylation to 2-methylhexanal are observed. The isomerization rate decreases as 2-methylhexanal and hexane formation rates proceed through a maximum. Heptanal is first detected after 10 h and hydrogenation of the linear aldehyde to heptanol is noticeable after 20 h (not shown in Fig. 2. Table 3 gives the XPS and CA data for the RhCaA as synthesized, after precarbonylation, and after exposure to the reaction environment.

The reaction start-up profiles for the synthesized RhCaA subjected to the three pretreatment/start-up sequences previously described are similar to those shown in Fig. 2. However, the time required to reach steady-state is 30, 40, and 30 h for sequences (i), (ii), and (iii), respectively. Cation-exchanged RhCaA also produced start-up behavior similar to that shown in Fig. 2 (steady-state in 30 h). A summary of the steady-state reaction rates for these experiments is given in Table 4.

TABLE 3

XPS and CA Data for Synthesized RhCaA

Condition of RhCaA	wt% Rh	Rh_{3d}/Si_{2p}		XPS/CA	Si_{2p}/Al_{2p}		XPS/CA
		XPS	CA		XPS	CA	
After synthesis	1.20	0.0115	0.0202	0.57	1.18	1.07	1.10
After pretreatment	0.80	0.0136	0.0134	1.01	1.54	1.08	1.43
After reaction	0.76	0.0033	0.0125	0.26	1.40	1.12	1.25

Note. Pretreatment: precarbonylation at 120°C and 3 atm for 12 h; reaction conditions: 1-hexene hydroformylation at 150°C and 2 atm for 33 h.

TABLE 4

Steady-State Rates of Various Catalysts Activated from Different Pretreatments

Products	Rate of formation (mol/g Rh h)			
	Synthesized RhCaA : (i)[a]	Synthesized RhCaA : (ii)	Synthesized RhCaA : (iii)	Cation-exchanged RhCaA : (i)
Hexane ($\times 10^3$)	6.0	8.0	6.0	14
Hexene isomers	0.09	0.10	0.07	0.09
2-Methylhexanal ($\times 10^4$)	4.5	4.1	1.8	5.3
Heptanal ($\times 10^3$)	1.9	2.0	0.8	1.6
2-Methylhexanol ($\times 10^4$)	—	—	—	0.8
Heptanol ($\times 10^3$)	0.8	0.7	—	1.2

Note. Synthesized RhCaA: 1.2% Rh; cation-exchanged RhCaA: 3.07% Rh.
[a] Pretreatment/start-up sequence (see text).

A precarbonylated, RhCaA (synthesized) catalyst which had reached steady-state at 1-hexene hydroformylation conditions was exposed to 4-methyl-1-pentene. The N_2 flow was reduced to maintain a constant total flow rate. The mixed olefin reactant composition was 3/1/1/1/1 H_2/1-hexene/4-methyl-1-pentene/CO/N_2. The steady-state reaction rates obtained from the mixed olefin feed are given in Table 5. If cyclohexylmercaptan is injected into the reactor, all catalytic activity ceased. However, after 15 h, isomerization and trace hydroformylation are noticeable. Finally, if the reactor temperature is raised to 200°C in an attempt to promote activity, isomerization increases dramatically but hydroformylation remains low. When cation exchanged RhCaA is exposed to the above-mentioned sequence, similar results are obtained. The chemical analyses of these catalysts before and after reaction are given in Table 6.

DISCUSSION

Liquid-phase hydroformylation. Table 1 shows the results obtained from 1-hexene hydroformylation by cation-exchanged and synthesized rhodium zeolite A catalysts. Since only trace conversion occurs with the synthesized RhNaA and RhKA most of the rhodium in these preparations must be intrazeolitic. This is because 1-hexene cannot penetrate the 3 and 4 Å pores of KA and NaA, respectively (*22*). However, some extracrystalline rhodium must still be present even after exchange with the various chloride salts. When the pore size of

TABLE 5

Steady-State Reaction Rates with Synthesized RhCaA (1.2% Rh)

Product	Rate of formation (mol/g Rh h)	
	1-Hexene feed	1-Hexene and 4-methyl-1-pentene feed
Hexene isomers	0.09	0.08
2-Methylhexanal ($\times 10^4$)	4.5	3.2
Heptanal ($\times 10^3$)	1.9	1.8
Heptanol ($\times 10^3$)	0.8	0.99
5-Methylhexanal ($\times 10^3$)	—	1.4
2,4-Dimethylpentanal ($\times 10$)	—	2.8
4-Methyl-1-pentene isomers	—	0.02

Note. T = 150°C, 2 atm total pressure.

TABLE 6

Chemical Analysis of RhCaA Catalysts

Catalyst	Si/Al	Rh/Si	wt% Rh
Untreated cation-exchanged RhCaA	0.95	0.055	3.07
After reaction cation-exchanged RhCaA	0.91	0.032	1.72
Untreated synthesized RhCaA	1.07	0.0202	1.20
After reaction synthesized RhCaA	0.90	0.0164	0.89

Note. Reaction conditions: 1-hexene hydroformylation at 150°C, mixed olefin (1-hexene + 4-methyl-1-pentene) hydroformylation at 150°C, injection of cyclohexylmercaptan at 150°C, mixed olefin hydroformylation at 200°C.

the synthesized rhodium zeolite A is increased to 5 Å (RhCaA) significant activity results. Table 1 also presents data that show the effect of H_2/CO. Hydroformylation activity increases with H_2/CO in the range of 1 to 3. This behavior has also been reported for the homogeneous hydroformylation of 1-hexene by $HRh(CO)(PPh_3)_3$ (*23*).

The activity of cation-exchanged RhCaA is significantly different from the synthesized RhCaA. The cation-exchanged RhCaA catalyst eluted the majority of its rhodium into solution and the observed catalysis is homogeneous. In (*9*) it was shown that the reactivity of cation-exchanged RhCaA was the same as $Rh_6(CO)_{16}$. This observation can also be made by comparing the exchanged RhCaA data in Table 1 to that for $Rh_6(CO)_{16}$ in Table 2. Since we could not detect rhodium in the liquids contacted with the synthetic RhCaA preparations listed in Table 1, most of the observed catalysis in these cases are probably from rhodium associated with the zeolite.

A 0.96% Rh RhCaA catalyst was synthesized in order to raise the probability of observing rhodium loss from the zeolite. When this catalyst was reacted at 1-hexene hydroformylation conditions, 0.01 m*M* rhodium was recovered in the reaction solution. The conversion was 0.26 and n/b was approximately 2.7. The addition of cyclohexylmercaptan to the 1-hexene hydroformylation system with RhCaA poisoned all activity. Therefore, rhodium must migrate from within the zeolite crystals to the surface under reaction conditions since most of the rhodium is initially within the zeolite. Also, the zeolite A must be in the calcium form to allow the rhodium species to migrate from within the crystals to the surface (see Table 1). Small amounts of the rhodium on the surface of the zeolite elute into solution. Thus, we believe that most of the observed catalysis occurs mainly via surface rhodium. This result also accounts for the production of 2-methylhexanal, a branched aldehyde. We suspect that the reason we do not observe rhodium elution from the synthesized RhCaA catalysts shown in Table 1 is that the amount is below our detection limits.

The absence of 2-ethylpentanal production by the synthesized RhCaA catalysts is not due to steric interactions of the rhodium with the zeolite. Rather, it is due to the level of conversion obtained with these catalysts. This conclusion is supported by the toluene data with $Rh_6(CO)_{16}$ in Table 2. Near complete conversion of 1-hexene must occur before 2-ethylpentanal is observed from the hydroformylation of the isomerized 1-hexene.

In an attempt to utilize intrazeolitic rhodium, the 0.96% Rh RhCaA catalyst was reacted at 120°C in the presence of cyclohexylmercaptan. Interestingly, only heptanal was produced with a 1-hexene conversion of 0.015. Thus, no isomerization of 1-hexene and no hydroformylation to branched aldehydes occurred. This experiment shows the ideal reaction selectivity obtained from the intrazeolitic rhodium. The RhCaA eluted rhodium during this conversion but its activity was poisoned by the cyclohexylmercaptan. The catalyst was filtered and used for three more batch experiments. Each experiment showed similar reactivity, and the rhodium content of the catalyst after each batch is shown in Fig. 1. After a significant initial loss of rhodium, only trace amounts were eluted.

Table 2 shows the effects of the solvent on homogeneous and heterogeneous hydroformylation. For $Rh_6(CO)_{16}$ in toluene, 1-hexene is consumed in approximately 3.25 h, while 22 h of contact are required to convert the 2- and 3-hexenes formed by isomerization. Thus, as 2 and 3-hexene are hydroformylated, n/b decreases to its final value of ca 0.8. The fact that terminal olefins react faster than internal olefins with homogeneous rhodium catalysts is known (*24*). No reactivity is observed with $Rh_6(CO)_{16}$ in a methanol solvent. This result is surprising since methanol has been shown to be an effective solvent for 1-hexene hydroformylation with homogeneous cobalt catalysts (*25*). Rhodium–silica also shows very little activity toward hydroformylation when using methanol. On the other hand, $HRh(CO)(PPh_3)_3$ and our synthesized RhCaA convert 1-hexene in methanol as well as in toluene, although the product distribution is slightly altered. Methanol apparently inhibits the formation of active species (presumably a hydride-containing complex) from $Rh_6(CO)_{16}$ and rhodium–silica. $HRh(CO)(PPh_3)_3$ already contains a rhodium hydride, and this may be the reason it remains active in methanol. Since cation-exchanged RhCaA is not active in methanol, and since methanol is small enough to penetrate the pore structure of CaA, it is not known why the synthesized RhCaA remains active in methanol.

Vapor-phase hydroformylation. Figure 2 shows the changes in activity with process time for a precarbonylated, synthesized RhCaA catalyst. Initially, isomerization is large and hydrogenation of 1-hexene and hydroformylation to 2-methylhexanal are observed. The isomerization rate decreases as 2-methylhexanal and hexane formation rates proceed through a maximum. Heptanal production increases until steady state is reached in approximately 30 h. As the concentration of heptanal rises, hydrogenation to heptanol occurs (heptanol only observed for $t > 20$ h). The branched aldehyde probably is hydrogenated also, but since its concentration is low, the 2-methylhexanol concentration is probably below detection limits.

Examination of the XPS/CA analyses shown in Table 3 gives insight to the fate of the rhodium. Initially, the superficial to bulk ratio of Rh/Si is 0.57. This value is expected since the synthesized RhNaA is exchanged with $CaCl_2$. The Ca^{2+} should replace surface Rh^{3+}. However, the superficial-to-bulk ratio will never reach zero since the XPS analysis is of the top 30 Å or so of the crystals. After carbonylation, a third of the total rhodium is lost (1.2 to 0.8% Rh). Also, notice that the superficial-to-bulk Rh/Si ratio has increased to 1.01. These data indicate that during carbonylation rhodium migrates to the surface of the zeolite and is lost into the flowing CO. Upon exposure to 33 h of 1-hexene hydroformylation the superficial-to-bulk Rh/Si ratio decreased to 0.26 while the bulk value of rhodium remained essentially unchanged. Also, during carbonylation and reaction, there appears to be a higher superficial ratio of Si/Al to that observed from the untreated RhCaA.

Rhodium carbonyls could be volatile under pretreatment and reaction conditions. If so, rhodium could be lost from the surface of the zeolite by sublimation as a carbonyl. Under reaction conditions (150°C, 2 atm) rhodium carbonyls would sublime faster than under carbonylation conditions (120°C, 3 atm). Thus, during carbonylation rhodium could migrate to the surface and sublime as a carbonyl, and this phenomena would account for the lowering of the bulk rhodium content and also the XPS/CA ratio obtained at the end of carbonylation. Under reaction conditions, rhodium may be sublimed faster than it can migrate to the surface and therefore the superficial/bulk ratio would be less than that obtained after carbonylation. Also, the migration of rhodium is probably greatly impaired by adsorbed hexene, hexane, linear aldehydes, and linear alcohols from the reactant/product mixture.

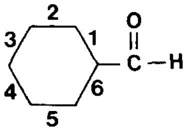
The reaction start-up profiles for the synthesized RhCaA subjected to the three pretreatment/start-up sequences previously described are similar and appear as shown in Fig. 2. However, the time required to reach steady state varied with the sequence and was 30, 40, and 30 h for sequences (i), (ii), and (iii), respectively. The predominant conversion was the isomerization of 1-hexene, especially at early times. The zeolite may be responsible for at least part of the observed isomerization activity. Blank CaA was able to promote 1-hexene isomerization at 150°C, 2 atm. However, the distribution of the isomers was not the same as with RhCaA. It is most probable that isomerization occurred from both the zeolite and the rhodium. It is peculiar that 2-methylhexanal and hexane proceed through a maximum during start-up. This behavior has been observed for other catalysts (*4*, *7*), and the decrease in production has been attributed to metal loss during the activation process (*4*). Since the cation-exchanged RhCaA proceeds through similar maximums in activity (*vide infra*) and since the amount of surface rhodium on this preparation is large in comparison to the synthesized RhCaA, it is doubtful that the maximums observed in reaction rates for these catalysts are consequences of rhodium loss. At steady-state the reactivity of the synthesized RhCaA is essentially independent of the pretreatment/start-up sequence (see Table 4). The sequences (i) and (iii) involve a pretreatment prior to reactant exposure. Therefore, these sequences provide time for the rhodium to begin migrating toward the surface of the zeolite while sequence (ii) does not. The lack of pretreatment time in sequence (ii) is probably the reason this procedure requires the longest time to reach steady-state.

The cation exchanged RhCaA gave start-up profiles similar to those shown in Fig. 2, and the steady-state rates are listed in Table 4. The behavior of exchanged RhCaA is essentially the same as the synthesized RhCaA. Since the amount of rhodium on the surface of the exchanged RhCaA is very large compared to the synthesized RhCaA, the amount of rhodium which is active must be very small. Also, since the superficial-to-bulk ratio of rhodium is low for the synthesized RhCaA, the rhodium utilization on both preparations must be low. The state of the inactive rhodium has not yet been determined.

The production of 2-methylhexanal from the synthesized RhCaA is a good indication that at least some of the observed catalysis is occurring on the surface of the zeolite. A mixed olefin feed consisting of 1-hexene and 4-methyl-1-pentene was reacted with the synthesized RhCaA and the steady-state rates are given in Table 5. Since the branched methyl group of the 4-methyl-1-pentene will not allow this olefin to penetrate the zeolite pore structure all of its activity must come from surface rhodium. From Table 5 it is shown that 4-methyl-1-pentene reacts similarly to the 1-hexene on the synthesized RhCaA. When cyclohexylmercaptan was injected into the reactor all activity for 4-methyl-1-pentene as well as 1-hexene ceased. Therefore, all the catalysis must be occurring on the surface of the zeolite. After 15 h, isomerization and trace hydroformylation returned probably due to the migration of rhodium from inside to the surface of the zeolite. Next, the reactor temperature was raised to 200°C in an attempt to promote activity. Isomerization increased dramatically while the hydroformylation activity remained small.

The cation-exchanged RhCaA was exposed to the same reaction sequence described in the previous paragraph, and similar results were obtained. The chemical analyses of the exchanged and synthesized RhCaA catalysts used in these experiments are given in Table 6. Both preparations lost significant amounts of rhodium.

One interesting result that can be obtained on any RhCaA preparation involved the hydroformylation of cyclohexene at 150°C, 2 atm. The expected hydroformylation product is cyclohexylcarboxaldehyde as shown below:



When cyclohexene is hydroformylated with RhCaA, cyclohexylcarboxaldehyde and heptanal are produced in a 1 : 1 ratio. It is interesting to note that no 2-methylhexanal is observed. This result suggests that cyclohexene forms an acyl intermediate with a rhodium complex after which carbon–carbon bond breakage occurs at positions 1 or 6. If the carbon–carbon bond breakage occurs before acyl formation, 2-methylhexanal would be expected to form in a ratio with heptanal similar to that observed from 1-hexene hydroformylation.

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