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A Comparison of X and Y Zeolite-Supported Rhodium as Propylene Hydroformylation Catalysts

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A direct comparison of rhodium-exchanged zeolites X and Y as vapor-phase propylene hydroformylation catalysts is reported. Hydrogenation and hydroformylation occur simultaneously over these catalysts in a reactant stream consisting of propylene : H_2 : N_2 : CO (3 : 3 : 2 : 1) at atmospheric pressure. Selectivity to *n*-butyraldehyde versus iso-butyraldehyde is 2.0 : 1 and 1.9 : 1 for rhodium on X and rhodium on Y, respectively. Similar hydroformylation activation energies are obtained, while hydrogenation activation energies are somewhat different. Infrared spectroscopy shows the presence of a geminal dicarbonyl, $Rh(CO)_2^+$, on zeolite X and $Rh_6(CO)_{16}$ on zeolite Y after hydroformylation.

INTRODUCTION

Homogeneous catalysis involving transition metal complexes are an integral part of the chemical industry. Two important industrial processes that rely on homogeneous catalysts are methanol carbonylation and olefin hydroformylation. Within the past 20 years, the well-established cobalt processes (*1, 2*) have been challenged by rhodium catalyst systems (*3, 4*). Today, a large fraction of the acetic acid produced is based on the rhodium carbonyl iodide catalyst reported by Paulik and Roth (*5*). Reasons behind the move to rhodium catalysts include greater catalyst activity and selectivity over their cobalt counterparts.

Catalyst deactivation and loss can be an expensive problem with homogeneous noble metal catalysts such as rhodium. Thus, widespread interest has focused on immobilizing rhodium catalysts in order to combine their high activity and selectivity with the processing advantages of a heterogeneous catalyst. Numerous immobilization techniques have been developed, and a review has recently appeared (*6*). The method of interest to this study is the incorporation of rhodium into zeolites by simple ion exchange. Several reports have shown that this method of anchoring rhodium leads to active carbonylation (*7–17*) and hydroformylation (*18, 19*) catalysts.

Vapor-phase carbonylation of methanol is the reaction that has received the most attention for rhodium-exchanged zeolites. Nefedov *et al.* (*7, 8*), Yamanis *et al.* (*13*), and Scurrell *et al.* (*9–12*) used rhodium-exchanged zeolite X (NaX), while Yashima *et al.* (*15*), Takahashi *et al.* (*16*), and Gelin *et al.* (*14*) used rhodium-exchanged zeolite Y (NaY) for carbonylation. A direct comparison of rhodium-exchanged X and Y zeolites is difficult to make since no one laboratory has studied the same reaction over similarly prepared X and Y zeolites. In spite of a lack of uniformity in catalyst preparation techniques, the following results have been reported for methanol carbonylation in the presence of a rhodium-exchanged X and Y zeolites: (a) during start-up, steady state was achieved in approximately 2 h (*15, 13*), (b) the rate of methyl acetate formation was

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first order with respect to methyl iodide partial pressure (*16, 17*), (c) activation energies of 13 4 (*16*) and 16 7 kcal/mol (*11*) were reported, however, Yamanis *et al* (*13*) showed that these data were probably strongly influenced by diffusional limitations, (d) catalyst deactivation occurred at 250°C (*7, 8*) and at 242°C (*13*) for RhNaX, while for RhNaY deactivation occurred at 200°C (*15*), (e) deactivation showed a nonzero order dependence for RhNaY (*15*) and a zero-order dependence for RhNaX (*13*) Results (a)–(c) show common behavior of the rhodium-exchanged X and Y zeolites, while (d) and (e) illustrate that some trends appear to be due to the presence of the zeolite type One possible explanation for observations (d) and (e) is that the X framework lends greater stability to the rhodium complex active for carbonylation

Previous work on the hydroformylation of olefins has only utilized rhodium-exchanged zeolite Y (*18, 19*)

The X and Y zeolites are topologically the same but differ in chemical composition For NaX Na_{86} $[(AlO_2)_{86}(SiO)_{106}]$ 264 H_2O and NaY $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$ 250 H_2O (20), the extra framework cations show different distributions over available sites (*21*) Electrostatic potentials and fields have been calculated for purely ionic models of X- and Y-type zeolites (*22, 23*) From these results, it was concluded that electrostatic fields of the magnitudes calculated should cause shifts of the bonding electrons in adsorbed molecules (*23*) Thus, while the spatial constraints on reacting species are the same in zeolites X and Y, the intrazeolite chemistry can be affected by the differences in electrostatic environments

The objective of this investigation is to compare the behavior of rhodium-exchanged NaX and NaY (exchanged under identical conditions) as propylene hydroformylation catalysts in order to study the effects of the zeolite support Infrared spectroscopy data were also obtained to shed light onto the nature of the active species

EXPERIMENTAL

Materials Rhodium trichloride trihydrate was obtained from AESAR Inc Zero-grade nitrogen and hydrogen were obtained from AIRCO, and zero-grade carbon monoxide was obtained from Matheson Company All of these gases were purified to remove trace oxygen and water before entering the reactor Propylene was purchased from Matheson Company and was used without further purification The zeolites used were Molecular Sieve 13X or 13Y purchased in powder form from the Linde Division of Union Carbide Corporation

Preparation of catalyst Following is a detailed description for the preparation of the rhodium-exchanged zeolites used in this study The procedure follows that of Arai and Tominaga (*19*) Zeolite powder (10 g) was washed with distilled water and dried in air at 120°C for 24 h The powder was then slurried in 200 ml 0 1 *N* NaCl solution at 95°C A 225-ml solution containing 1 0 g $RhCl_3$ $3H_2O$ was added dropwise over 2 h to the zeolite slurry The pH of the slurry was monitored every 10 min By addition of 0 1 *N* NaOH, the pH was maintained at 6 0 When the addition of the rhodium solution was completed, the zeolite slurry was stirred for 5 h at 95°C, after which it was allowed to cool overnight The zeolite was filtered, washed with 1 5 liters of distilled water, then dried in air at 150°C to a free flowing powder The rhodium content for RhNaX was 2 7 wt% and for RhNaY it was 3 4 wt% These will be referred to as catalysts (a) and (b), respectively

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 5 g of catalyst was loaded into the reactor

For the infrared work, samples were prepared as KBr disks in a Vacuum Atmospheres Dry Box under a nitrogen atmosphere Variations in KBr disk preparation technique had no effect on the carbonyl region of the spectrum Selected preparations were also recorded as mulls in mineral oil These were identical in the carbonyl stretching region to the samples recorded as KBr pellets Thus, localized heating during the fusion of KBr did not alter the carbonyl species Infrared studies were performed with a Nicolet MX-1 Fourier Transform Infrared Spectrometer

Reactor system and procedure The hydroformylation of propylene was carried out in a differential fixed bed reactor at near atmospheric total pressure The reactor itself was made of a stainless-steel tube, 6 35-mm o d , 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 better than ±0 5°C The catalyst bed was preceded and followed by sections of glass wool

The reactor start-up began by purging the system with nitrogen to remove air The catalyst was precarbonylated by introducing CO into the reactor at 15–20 cm^3/min (STP), then pressurizing to 3 atm The catalyst was maintained at 120°C under the flowing CO for 8–10 h The reaction mixture, which consisted of a 3/3/2/1 mixture of H_2/olefin/N_2/CO (H_2 flow rate = 15 cm^3/min STP), was then introduced into the system Nitrogen was included in the feed stream to allow for partial pressure variations of the reacting species at constant contact time

Gas chromatographic analysis was achieved by using two chromatographs In chromatograph A, *n*- and iso-butyraldehyde were separated and analyzed with a Porapak S column at 145°C using a nitrogen carrier gas flowing at the rate of 35 cm^3/min (STP) Chromatograph B was used to separate propane from propylene with a Porosil B column at 70°C using a nitrogen carrier gas flowing at the rate of 35 cm^3/min (STP) Flame ionization detectors were used in both chromatographs

Noncatalytic carbonylation reactor system Noncatalytic carbonylations of the rhodium-exchanged zeolite powder were performed in a Parr minireactor Temperature control was ±5°C Samples from this reactor were used for obtaining infrared spectroscopy data used to approximate the state of the rhodium zeolite after pretreatment of CO, but prior to exposure of hydroformylation conditions

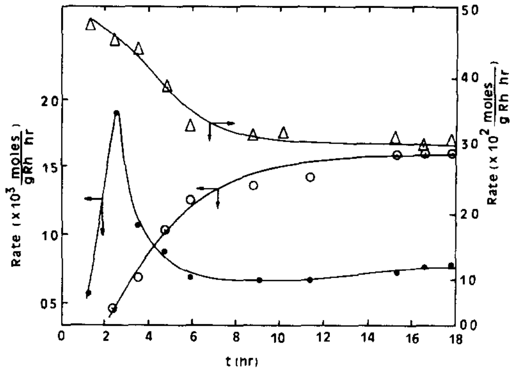

FIG 1 Reaction rates versus process time for RhNaX Reaction conditions 150°C, 1 atm (△) Propane, (●) iso-butyraldehyde, (○) normal-butyraldehyde

RESULTS

In order to bring about hydroformylation, contact with reactants required a minimum temperature of 150°C after which activity could be maintained at lower temperatures Figure 1 shows the changes in activity with process time for the RhNaX catalyst The process time is shown to begin when the catalyst bed reached 150°C Notice that hydrogenation activity declines as hydroformylation activity increases, and that the rate of iso-butyraldehyde goes through a maximum Steady state is achieved at approximately the same time for all three components In Fig 2, the changes in activity with process time for the RhNaY catalyst are illustrated The behavior of RhNaY is qualitatively the same as with RhNaX except that the rate of iso-butyraldehyde does not go through as sharp a maximum In all cases, once steady state is achieved, it can be maintained for 20 h of operation

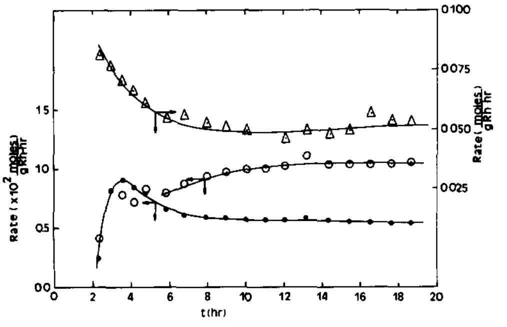

FIG 2 Reaction rates versus process time for RhNaY Reaction conditions 150°C, 1 atm (△) Propane, (●) iso-butyraldehyde, (○) normal-butyraldehyde

Tables 1 and 2 summarize the reactivity data, the data are completely reproducible For catalysts (a) and (b) the activation energies for hydroformylation and the regioselectivity (*n*/*i*) are approximately the same Figure 3 shows a representative plot of the temperature effects on reaction rates from which the activation energies are calculated In all cases, the activation energy plots show no curvature The hydrogenation activation energy increases when going from catalyst (b) to (a) as does the selectivity to hydrogenation Catalyst (c) was pretreated with pure H_2 to reduce the rhodium to metal When a propylene–hydrogen mixture is passed over the reduced RhNaY complete conversion to propane is observed Since it is well known that rhodium metal is an excellent hydrogenation catalyst, we feel that this test confirms that rhodium is present in the metallic state Upon introduction of the hydroformylation reaction mixture only hydrogenation occurs The results of Arai and Tominaga are also included in these tables for comparison Their catalysts behave substantially different from those made in our laboratory

The effect of contact time (*W*/*F*) on the conversions of propylene to propane, ξ_H, and aldehydes, ξ_N and ξ_I, are shown in Fig 4 In the region of *W*/*F* lower than 5 g-h/mol the conversions where proportional to the contact time

TABLE 1

Catalytic Results of Propylene Hydroformylation and Hydrogenation over RhNaX and RhNaY

Zeolite	Pretreatment	Product	Rate[a] $\left(\frac{\text{mol}}{\text{g Rh h}}\right)$	E[b] (kcal/mol)
(a) RhNaX	CO as described in text	C_3H_8	$2\ 8 \times 10^{-2}$	25 1
		n C_4H_8O	$1\ 6 \times 10^{-3}$	9 7
		i C_4H_8O	$0\ 8 \times 10^{-3}$	11 7
(b) RhNaY	CO as described in text	C_3H_8	$5\ 3 \times 10^{-2}$	21 0
		n-C_4H_8O	$1\ 0 \times 10^{-2}$	9 2
		i-C_4H_8O	$5\ 4 \times 10^{-3}$	11 4
(c) RhNaY	0 5 h exposure to H_2 at 100°C	C_3H_8	$2\ 3 \times 10^{-7}$	18 0[c]
		n C_4H_8O	—	—
		i C_4H_8O	—	—
RhNaY[d] (from (*19*))	Not reported	C_3H_8	$7\ 0 \times 10^{-2}$	24 2[e]
		n C_4H_8O	$1\ 0 \times 10^{-3}$	8 7[e]
		i C_4H_8O	$0\ 9 \times 10^{-4}$	7 3[e]

[a] At 150°C 1 atm

[b] At 120–150°C

[c] At 110–150°C

[d] Rh 3 7 wt% −10/+20 mesh particles contact time twice as long as the present study

[e] At 130–170°C

TABLE 2

Selectivity Results for RhNaX and RhNaY at 150°C at 1 atm

Zeolite	Catalyst pretreatment	Selectivity hydrogenation/ hydroformylation	Regioselectivity (*n*/*i*)
(a) RhNaX	CO as described in text	11 7	2 0
(b) RhNaY	CO as described in text	3 44	1 9
RhNaY (from (*19*))	Not reported	37 6	1 2

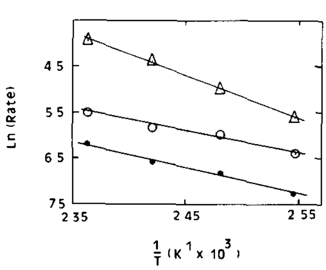

FIG 3 Effects of temperature on reaction rates for RhNaY (△) Propane, (●) iso-butyraldehyde, (○) normal-butyraldehyde

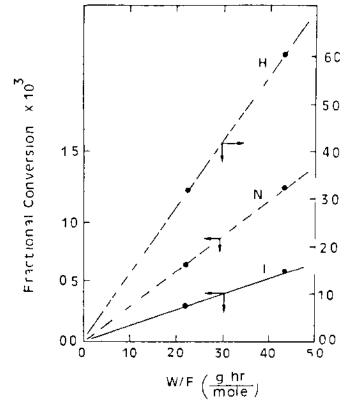

FIG 4 Dependence of conversion on W/F, where W is the mass of catalyst and F is the total molar flow rate

Infrared spectra for (a) and (b) are plotted in Figs 5 and 6, respectively Spectra prior to and after hydroformylation are shown

DISCUSSION

The RhNaX and RhNaY (catalysts (a) and (b) described above) are active for hydrogenation and hydroformylation of propylene at atmospheric pressure Hydroformylation activity is initiated only when the catalysts contact reactants at 150°C It is interesting to note that Scurrell and Howe (*11*) reported the same temperature requirement to activate RhNaX for methanol carbonylation They postulated that the activation process involved the reduction of Rh^{+3} to Rh^{+1} Catalysts (a) and (b) were both pretreated with CO at 120°C This treatment leads to reduction of rhodium from Rh^{+3} to Rh^{+1} or Rh^0 (*vide infra*) Thus, the activation temperature associated with hydroformylation activity cannot be due to chemical reduction Once steady state is reached it can be maintained for as long as 20 h indicating that deactivation and/or rhodium loss does not occur after steady-state has been reached

RhNaX and RhNaY show similar hydroformylation behavior, i e , activation energies and regioselectivity The activation energy corresponding to the formation of iso-butyraldehyde was slightly larger than that corresponding to the formation of *n*-butyraldehyde Therefore, the regioselectivity increases as the temperature decreases This trend has also been observed in homogeneous hydroformylations (*24*) Because of the relatively low values of the hydroformylation activation energies, one might suspect the influence of mass transfer In Fig 4 we show that the conversions are proportional to the contact time, thus validating the differential analysis used to calculate the rates Figure 3 illustrates the temperature dependence of the rates These graphs show no curvature over the temperature range of 120 to 150°C The absence of curvature in these figures suggest that mass transfer is not controlling the re-

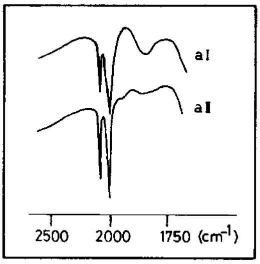

FIG 5 Spectra of RhNaX (a) (aI) After CO pretreatment, (aII) after hydroformylation conditions

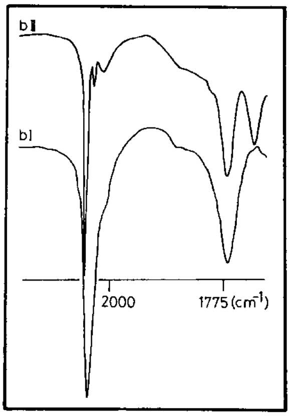

FIG 6 Spectra of RhNaY (b) (bI) After CO pretreatment, (bII) after hydroformylation conditions The absorption at 1710 in (bII) is assigned tentatively to aldehyde present within the zeolite This band is present in all samples after hydroformylation

action rates (*25*) The *n*/*i* ratio at 150°C obtained from the RhNaX and RhNaY catalysts was 2 0 and 1 9, respectively For the homogeneous hydroformylation of propylene by binary rhodium carbonyls, the reported regioselectivity is less than or equal to one (*26*) The increase in regioselectivity observed here must be due to the influence of the zeolite Since the pore size of zeolites X and Y is significantly larger than either reactants or products, we feel that the enhanced selectivity is due to steric and/or electronic influences of the zeolite at the active site rather than "molecular sieving " The catalysts may thus be considered to be zeolite-modified rhodium carbonyls, i e , the framework serves as a ligand for rhodium, rather than merely as a support for a binary rhodium carbonyl In light of the similar hydroformylation behavior of (a) and (b), we propose that the same active species is present on each catalyst

In contrast to hydroformylation, the hydrogenation behavior of each catalyst is different The activation energy obtained from RhNaX is 4 kcal/mol larger than that for RhNaY, and neither is equivalent to that of rhodium metal on zeolite Y Since the activation energies of RhNaX and RhNaY are larger than for rhodium metal on zeolite Y, we suspect that if rhodium metal is present on RhNaX or RhNaY, its concentration is small, and does not significantly contribute to the observed hydrogenation behavior The difference in activation energy for hydrogenation (4 kcal/mol) on (a) and (b) is significant compared to the error, and is reproducible for separate catalyst runs Thus, it is probable that each catalyst has a different species active for hydrogenation

A RhNaY catalyst (active at 150°C) when cooled to 120°C and left overnight under flowing CO at a pressure of 3 atm immediately regained hydroformylation activity when reactants were introduced at 120°C and 1 atm At 150°C the catalyst behavior returned to that obtained on the previous day Thus, the hydroformylation active species is stable at 120°C under a CO blanket

The similarity in activity for hydroformylation over (a) and (b) is in striking contrast to the predominant species present in each as identified by infrared spectroscopy On RhNaX, (a), after precarbonylation but before hydroformylation infrared spectroscopy shows the presence of at least two species (see Fig 5) One of these is assigned to $Rh(CO)_2{}^{+}$-NaX, which gives rise to absorptions at 2093 and 2010 cm^{-1} This species is well defined for supported rhodium carbonyls (*12, 13, 27*) Other species give broad absorptions at ~2010 and 1845 cm^{-1} The second band is in the region of a bridging carbonyl, thus indicating the presence of rhodium clusters After hydroformylation infrared spectroscopy shows nearly the exclusive presence of the geminal dicarbonyl, $Rh(CO)_2{}^{+1}$–NaX

On RhNaY, (b), after precarbonylation and after hydroformylation infrared spectroscopy shows nearly exclusive formation of the rhodium cluster, $Rh_6(CO)_{16}$ (see Fig 6) This assignment is based on the position of the ir bands observed (2096, 2060, 1770 cm^{-1}, bII) compared to those reported for rhodium clusters synthesized by a separate route on Y zeolites (*18, 28*) It is not clear at this time why the X zeolite stabilizes a Rh^{+1} complex while the Y zeolite favors rhodium clusters which contain Rh^0

Three lines of evidence lead us to speculate on the nature of the active species for hydroformylation (i) Hydrogenation activity decreases as hydroformylation activity increases Furthermore, steady state is reached at the same time for hydrogenation and hydroformylation This is consistent with conversion of the species active for hydrogenation into an active hydroformylation species Complete conversion may be limited by an equilibrium between the two species (ii) X and Y zeolite-supported rhodium catalysts behave identically within experimental error for hydroformylation while hydrogenation is slightly different Infrared spectroscopy shows RhNaX and RhNaY to contain different rhodium carbonyl complexes, i e , $Rh(CO)_2{}^{+}$–NaX and

$Rh_6(CO)_{16}$–NaY These may show different hydrogenation activity yet transform to yield the same hydroformylation catalyst Finally (iii) homogeneous olefin hydroformylation catalysts (cobalt or rhodium) contain a metal–hydrogen bond (*29*) Generation of a rhodium hydride may account for the observed 150°C activation temperature required to initiate hydroformylation Equations (1) and (2) represent viable pathways which can account for the evidence above

$$Rh(CO)_2^+\text{–NaX} \overset{H_2}{\rightleftharpoons} HRh(CO)_2\text{–NaX} + H^+\text{–NaX} \quad (1)$$

$$Rh_6(CO)_{16}\text{–NaY} \overset{H_2/CO}{\rightleftharpoons} HRh(CO)_2\text{–NaY} + Rh_5(CO)_{15}^-\text{–NaY} + H^+\text{–NaY} \quad (2)$$

Equation (1) has precedent in homogeneous systems involving rhodium carbonyl chloride complexes (*30*) Equation (2) does not have direct precedent but $Rh_5(CO)_{15}^-$ is a well-defined cluster (*31*)

The results of Arai and Tominaga (*19*) have been included in Tables 1 and 2 for comparison Although we have followed their rhodium exchange procedure, their activation procedure is not reported They claim that their catalyst contains the geminal dicarbonyl $Rh(CO)_2^+$–NaY and that no Rh^0 was present If the dicarbonyl is the active species for hydrogenation on our RhNaX catalyst then Arai and Tominaga's hydrogenation activation energy compares favorably However, the catalysts prepared in our laboratory behave differently for hydroformylation Perhaps the most significant difference is Arai and Tominaga's observation of $Rh(CO)_2^+$–NaY In our hands, using the same cation-exchange procedure to introduce rhodium, only rhodium clusters are observed This is true for a wide range of catalyst carbonylation treatments (*32*) [3]

CONCLUSIONS

The present work has shown that the same hydroformylation behavior is obtained from RhNaX and RhNaY The influence of the zeolite is to increase the *n*/*i* ratio above that of binary rhodium carbonyls Although similar hydroformylation behavior is obtained from the X and Y zeolites, each stabilizes a different rhodium carbonyl at room temperature A geminal rhodium dicarbonyl species is observed on NaX while clusters predominate on NaY

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