

Vapor Phase Carbonylation of Methanol over Rh-Y Zeolite

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The carbonylation of methanol over Rh-Y zeolite catalyst in the presence of methyl iodide was studied at 423 to 473 K under atmospheric pressure. The catalytic activity of Rh-Y was much superior to other supported rhodium chloride catalysts such as $\text{RhCl}_3/\text{Al}_2\text{O}_3$, $\text{RhCl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{RhCl}_3/\text{SiO}_2$, and Rh-cation exchanged resin. Methyl acetate was the main product of this carbonylation, although the yield of acetic acid increased with contact time and the partial pressure of methyl iodide. The rate of methyl acetate formation increased with the content of Rh on the zeolite up to 0.6 wt%. For Rh-Y with more than 0.6 wt% of Rh, however, the rate decreased with the process time, and it was observed that the rhodium species fell off from the catalyst support system and the most zeolite framework was broken. During the first stage of the reaction, an induction period was observed which could be eliminated by calcining in nitrogen or helium at 473 K. However, the catalytic activity of Rh-Y was reduced by calcination at 573 K. When Rh-Y was calcined in hydrogen at 573 K, the catalyst had no activity. Therefore, it was concluded that the precursor of the active rhodium site was a trivalent rhodium which was firmly anchored on the zeolite by an ion exchange process, and that water molecules adsorbed in the zeolite prevented the formation of the active Rh site. The active Rh sites on Y zeolite were stable up to 473 K, but over 483 K was inactivated with an irreversible change.

INTRODUCTION

The synthesis of acetic acid from methanol and carbon monoxide has been an attractive process from the viewpoint of the chemical industry, and the reaction has been commonly catalyzed by a cobalt complex catalyst under severe conditions, such as 473 K and several hundred atm of carbon monoxide. Since the discovery of highly active and selective homogeneous rhodium complex catalysts for methanol carbonylation by Paulik and Roth (1), a new synthetic process for the production of acetic acid by using a rhodium complex

catalyst has been developed. The rhodium complex catalyst successfully accelerates this reaction under remarkably mild conditions in comparison with the cobalt complex catalyst. The reaction mechanism for this reaction system has been proposed (2, 3).

Homogeneous catalysts often show a high activity and selectivity. However, these catalysts are frequently not used in industrial processes, because the process of separating the products and catalyst from the reaction mixture is complicated, and a corrosion-resistant reactor must be used for corrosive catalyst solutions. These

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disadvantages can be eliminated by anchoring the homogeneous catalysts on a solid material. In this regard, some systems have been studied extensively, and the results have been reported (4-6). Homogeneous rhodium complexes for methanol carbonylation have been converted to heterogeneous systems and reported on by Schultz and Montgomery (7) and Robinson *et al.* (8) for the charcoal supported catalyst, or by Jarrell and Gates (9) for the polymer-bound catalyst.

Zeolite can anchor some transition metal cations in its framework by an ion exchange process. Transition metal cations supported on zeolite are more highly dispersed compared with a conventional impregnation on silica gel, alumina on other solid material. Moreover, zeolite has a higher thermal stability than organic polymer supports. Transition metal cations on zeolite often show a catalytic activity similar to transition metal complex catalysts. For example, Cr-Y zeolite effectively catalyzes ethylene polymerization in the same way as a chromia catalyst (10, 11), and Ni-Y zeolite shows catalytic activity for ethylene dimerization (10) which is also accelerated by a nickel oxide catalyst or a homogeneous nickel complex catalysts. Furthermore, Rh-Y zeolite, like homogeneous rhodium complex catalysts (12), remarkably promotes ethylene dimerization (10, 13). Recently, it has been reported that the carbonylation of methanol is catalyzed by Rh-X zeolite and that its catalytic behavior is similar to that of the homogeneous rhodium complex catalyst (14-16). In this paper, the carbonylation of methanol over Rh-Y catalyst is studied in detail, and some catalytic properties of Rh-Y and the possibility of the heterogenization of the rhodium complex catalyst by using zeolite are discussed.

EXPERIMENTAL

Materials. Rhodium trichloride trihydrate and rhodium trinitrate were ob-

tained from Nippon Engelhard Co. and Kanto Chemical Co., respectively. Rhodium sulfate was prepared by dissolving rhodium trihydroxide in sulfuric acid. The methanol and methyl iodide obtained from Wako Pure Chemical Ind. Ltd. were used without any further purification, and the carbon monoxide was obtained from Takachiho Chem. Ind. Co.

Linde SK-40 as a Y-zeolite, silica gel, silica-alumina, and alumina were obtained from commercial sources. The cation exchange resin Amberlite 200C, and the anion exchange resin Amberlyst A-26 were acquired from Japan Organo Co.

Preparation of catalysts. A rhodium cation-exchanged Y zeolite (Rh-Y) was prepared following a conventional cation exchange method at 353 K from SK-40 and a rhodium chloride aqueous solution controlled at pH 4.5 with sodium hydroxide. Under the same conditions, a rhodium cation exchange resin and a rhodium anion exchange resin were prepared. Other catalysts for which silica gel, silica-alumina, or alumina were used as supports were prepared by the usual impregnation method. The rhodium content of the catalysts was measured by atomic absorption spectrophotometry from sample of catalysts dissolved in a mixture of hydrofluoric and hydrochloric acids.

Apparatus and procedure. Methanol carbonylation was carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure. The catalyst was placed in a quartz reactor equipped with an electric heater, and the catalyst bed was purged for 2 hr with nitrogen at room temperature to remove the air in the system. After the catalyst bed was heated to the reaction temperature, methanol and methyl iodide were fed by a microfeeder and carbon monoxide was fed to start the carbonylation. Helium was used as a diluent gas. A small part of the reaction mixture was sampled directly through a silicon rubber plug with

a hot syringe and was analyzed by gas chromatography using a 4-m-long Chromosorb 101 column at 428 K.

RESULTS

It was found that Rh-Y zeolite had a remarkably high activity for the carbonylation of methanol in the presence of methyl iodide under atmospheric pressure at 443 K. Rhodium trichloride (1), monovalent rhodium complex (1, 17), charcoal-supported rhodium catalyst (7, 8), polymer-bound rhodium complex catalyst (9), and Rh-X zeolite (14-16) all catalyze the carbonylation of methanol in the presence of methyl iodide which is an excellent promotor, as has been reported by other researchers. This carbonylation needs a promotor, such as methyl iodide, hydrogen iodide, or pentachlorobenzethiol (18). In this work, methyl iodide was chosen as the promotor.

Comparisons were made of the formation rates of methyl acetate (r_{MA}) over Rh-Y zeolite, $RhCl_3/Al_2O_3$, $RhCl_3/SiO_2-Al_2O_3$, and $RhCl_3/SiO_2$ with the same rhodium content (4.3×10^{-5} g-atom/g), and Rh-cation exchange resin (3.6×10^{-5} g-atom/g). The changes of activity with

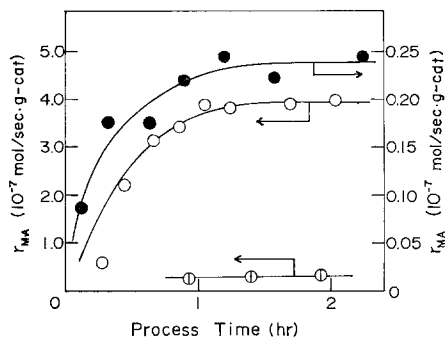


FIG. 1. Carbonylation activity change with process time. \circ , Rh-Y^a; \odot , $RhCl_3/Al_2O_3$ ^a; \bullet , Rh-cation exchange resin^b. Rh content, (a) 4.2×10^{-5} g-atom/g-cat; (b) 3.6×10^{-5} g-atom/g-cat. Reaction conditions: temperature, (a) 443 K; (b) 423 K. W/F, (a) 5.8×10^3 g-sec/mol; (b) 5.8×10^4 g-sec/mol. P_{MeOH} , 1.19×10^4 Pa. P_{CO} , 3.06×10^4 Pa. P_{MeI} , 1.19×10^3 Pa.

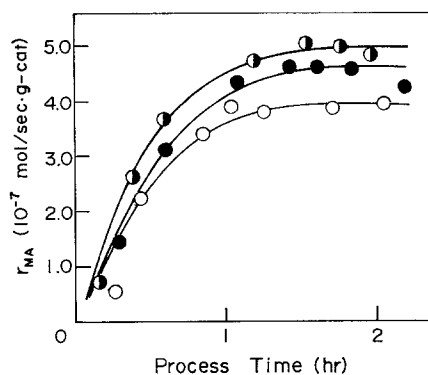


FIG. 2. Carbonylation activities of Rh-Y prepared from three rhodium sources. \circ , $RhCl_3$; \odot , $Rh(NO_3)_3$; \bullet , $Rh_2(SO_4)_3$. Rh content, 4.2×10^{-5} g-atom/g-cat. Reaction conditions: temperature, 443 K; W/F, 5.8×10^3 g-sec/mol; P_{MeOH} , 1.19×10^4 Pa; P_{CO} , 3.06×10^4 Pa; P_{MeI} , 1.19×10^3 Pa.

process time for the Rh-Y zeolite, $RhCl_3/Al_2O_3$, and Rh-cation exchange resin are shown in Fig. 1. However, little carbonylation activity was detected on the silica-alumina or silica-supported catalyst under our experimental conditions. Rh-Y showed the highest carbonylation activity among the catalysts investigated. On Rh-Y catalyst, it was observed that r_{MA} increased with process time during the early stage of the reaction, and after 1 hr maintained a constant value for more than 10 hr. The main products over the Rh-Y catalyst were methyl acetate and dimethyl ether, and more than 95 mol% of the methyl iodide fed into the reaction system was recovered from the reaction mixture collected with a dry ice trap. The Rh-cation exchange resin catalyst was active for this carbonylation of methanol, but it was much less active than the Rh-Y. Alumina supported rhodium chloride catalyst was more active for the carbonylation than the other two impregnated catalyst, i.e., $RhCl_3/SiO_2-Al_2O_3$ and $RhCl_3/SiO_2$. It was observed that almost no rhodium species fell off from the alumina supported catalyst. In contrast, a considerable amount of the rhodium species fell off as a red

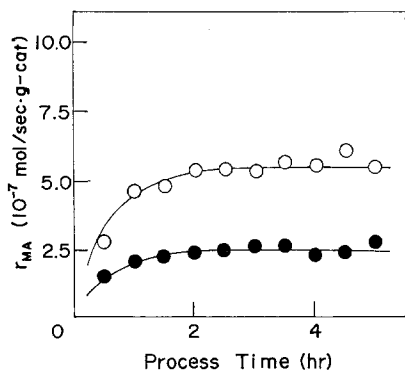


FIG. 3. Effect of rhodium content on methyl acetate formation rate with low content Rh-Y zeolites. O, 5.8×10^{-5} g-atom/g-cat; ●, 2.9×10^{-5} g-atom/g-cat. Reaction conditions are the same as shown in Fig. 2.

needle-like crystal from the silica gel and silica-alumina supported catalysts.

Three kinds of Rh-Y zeolites were prepared using three kinds of rhodium compounds, i.e., rhodium chloride, rhodium nitrate, and rhodium sulfate. The catalytic activities of these three Rh-Y zeolites are shown in Fig. 2. They showed almost the same activity in spite of having different counterions, which suggested that the active rhodium site was unaffected by the counterions for the rhodium cation.

The relationship between rhodium content in the Rh-Y zeolite catalyst and

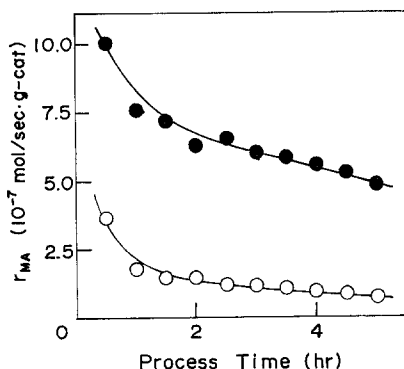


FIG. 4. Effect of rhodium content on methyl acetate formation rate with high content Rh-Y zeolites. O, 1.9×10^{-4} g-atom/g-cat; ●, 6.8×10^{-4} g-atom/g-cat. Reaction conditions are the same as shown in Fig. 2.

formation rate of methyl acetate is shown in Figs. 3 and 4 for the regions of relatively low and high rhodium contents, respectively. In the region of low rhodium content, the rate of methyl acetate formation gradually increased with process time during the early stage of the reaction, reached a steady value, and only a small amount of rhodium fell off from the catalyst. The catalytic activity at the steady state was approximately proportional to the rhodium content. However, Nefedov *et al.* reported that in the case of a Rh-X zeolite catalyst, the catalytic activity per Rh atom decreased considerably with increasing rhodium content in the zeolite (14). On the other hand, in the region of relatively high rhodium content, the rate of methyl acetate formation decreased considerably with process time and reached no steady state as shown in Fig. 4. On the Y type zeolite the amount of the effective rhodium did not exceed about a 6% degree of exchange (ca. 0.6 wt%) which corresponded to about two rhodium sites per unit cell of Y zeolite.

The effects of the calcination atmosphere on the rate of methyl acetate

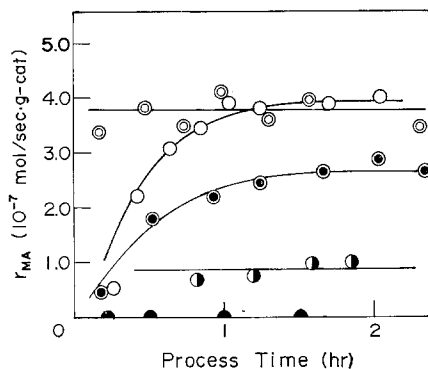


FIG. 5. Effect of various pretreatments of the Rh-Y catalyst on methyl acetate formation rate. O, exposed to an N_2 stream at room temperature for 2 hr; ◐, calcined in an He stream at 473 K for 2 hr; ◑, calcined in an He stream at 573 K for 2 hr; ◒, calcined in an H_2 stream at 573 K for 1 hr; ◓, added H_2O after calcination in an He stream at 473 K for 2 hr. Reaction conditions are the same as shown in Fig. 2.

formation are shown in Fig. 5. The Rh-Y zeolite catalyst with the usual treatment, i.e., exposure to a nitrogen stream at room temperature for 2 hr, had about a 1 hr induction period as shown in Fig. 1. This induction period disappeared when the Rh-Y was calcined at 473 K in a nitrogen or helium stream, and the catalyst calcined under these conditions showed a carbonylation activity as high as that of the usually treated catalyst at the steady state. However, this induction period reappeared when the Rh-Y was exposed to water vapor at room temperature for 2 hr after being calcined in He at 473 K for 2 hr. When Rh-Y was calcined in He at a higher temperature, such as 573 K, a lower catalytic activity for carbonylation was obtained. The Rh-Y reduced by H_2 at 573 K for 2 hr showed no carbonylation activity.

The effect of reaction temperature on the methyl acetate formation rate is shown in Fig. 6. The steady formation rate which was obtained at any given temperature increased with reaction temperature up to about 473 K. In this temperature range, the same rate was observed for fresh catalyst and catalyst which once had been used at another reaction temperature. Over 473 K, the formation rate decreased

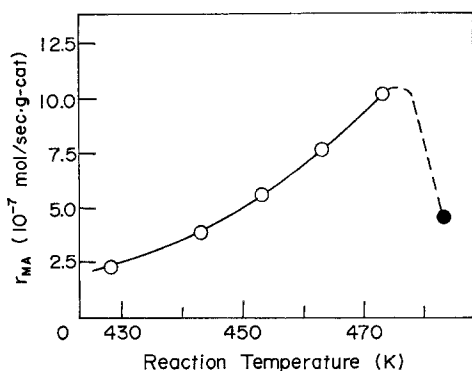


FIG. 6. Effect of reaction temperature on methyl acetate formation rate on Rh-Y. ○, r_{MA} at the steady state; ●, r_{MA} at 40 min of process time. Reaction conditions are the same as shown in Fig. 2 except for reaction temperature.

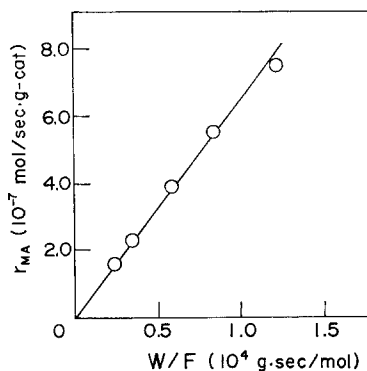


FIG. 7. Dependence of methyl acetate formation rate on W/F. Reaction conditions are the same as shown in Fig. 2 except for W/F.

with process time, and the activity of the catalyst, after being used, never showed the original value when the catalyst was used again at 443 K. However, removal of rhodium from the catalyst system was not detected at the higher reaction temperatures. These results suggest that an irreversible deactivation of the active site occurs at reaction temperatures higher than 473 K.

The effect of contact time (W/F) on the rate of methyl acetate formation is shown in Fig. 7. In the region of W/F lower than 8500 g-sec/mol, methyl acetate was the only product of carbonylation and its formation rate was proportional to W/F. With an increase of W/F, temperature, and partial pressure of methyl iodide, the formation of acetic acid became appreciable, and the ratio of acetic acid to methyl acetate increased with methanol conversion, as shown in Table 1. These results are in agreement with the results expected from the reaction mechanism, proposed in the homogeneous rhodium complex catalysis, in which an acetyl rhodium complex is a reaction intermediate (1-3).

DISCUSSION

Based on our results, the Rh-Y zeolite catalyst has a high activity for the car-

TABLE 1
Changes in Products Distribution with Methanol Conversion on Rh-Y^a

W/F (10 ⁴ g·sec/mol)	P _{MeI} /P _{MeOH} (mol/mol)	Reaction temperature (K)	MeOH conversion (mol%)	Yield (mol%)		
				AcOMe	AcOH	MeOMe
0.58	0.1	443	8.2	3.9	N.D.	4.3
0.63	0.3	453	60.8	53.8	0.5	6.3
1.25	0.3	453	87.7	76.6	7.4	3.7
3.92	0.3	443	98.5	75.3	22.6	0.6
7.85	0.3	443	99.7	68.3	30.0	1.4

^a Rhodium content: 4.2×10^{-5} g-atom/g-cat.

bonylation of methanol in the presence of methyl iodide, and the rhodium complex catalyst can be successfully heterogenized by Y type zeolite.

It is not clear whether zeolite anchors rhodium chloride by means of a cation exchange or an adsorption. Rhodium chloride was absorbed from its aqueous solution by zeolite, alumina, silica gel, or silica-alumina. Moreover, rhodium chloride was absorbed rapidly from its methanolic solution onto alumina or silica-alumina. If rhodium chloride is anchored on zeolite by an adsorption, it should also be anchored on zeolite from a methanolic solution in the same way as from the aqueous solution. However, rhodium chloride was hardly absorbed onto zeolite from the methanolic solution. So, it could be considered that the rhodium species were anchored on zeolite by an ion-exchange process. On the other hand, it has been found that rhodium chloride forms the anion $[\text{RhCl}_6]^{3-}$ in high concentrations of chloride ion (19). In our ion exchange experiments, rhodium species were anchored by an ion-exchange process on not only anion exchange resin (Amberlyst A-26) but also cation exchange resin (Amberlite 200C), and their rhodium contents per g-resin were 8.6×10^{-5} and 3.6×10^{-5} g-atom, respectively. Therefore, our aqueous rhodium chloride solution was expected to contain the series of rhodium species, $[\text{RhCl}_n]^{-(n-3)}$ ($n = 0-6$). The cation ex-

change resin catalyst was active for methanol carbonylation and its activity per Rh g-atom corresponded to about $\frac{1}{8}$ of that of the Rh-Y zeolite at the steady state (Fig. 1). However, the anion-exchange resin catalyst was inactive under the same reaction conditions in spite of its adequate rhodium content. It was observed that no rhodium compounds fell off from the catalyst system during the reaction. This anion exchange resin kept more than 90% of its original ion exchange capacity after using the system at 423 K for 2 hr, although the recommended operating limit for this resin in Cl⁻ form was 373 K. So, it was surmised that the lack of catalytic activity for the Rh-anion exchange resin was not caused by the thermal decomposition of the resin. From these results, it was concluded that a rhodium cation was anchored on the zeolite by cation exchange from the aqueous solution of rhodium chloride, and it was suggested that too many chloride ions combined with the Rh prevent the formation of the active sites for this carbonylation. However, the active site was scarcely affected by the counterion for the rhodium cation (Fig. 2).

The amount of the effective rhodium did not exceed about a 6% degree of exchange (ca. 0.6 wt%) as shown in Figs. 3 and 4. A considerable amount of rhodium fell off as red needle-like crystals from the high rhodium content zeolites. However,

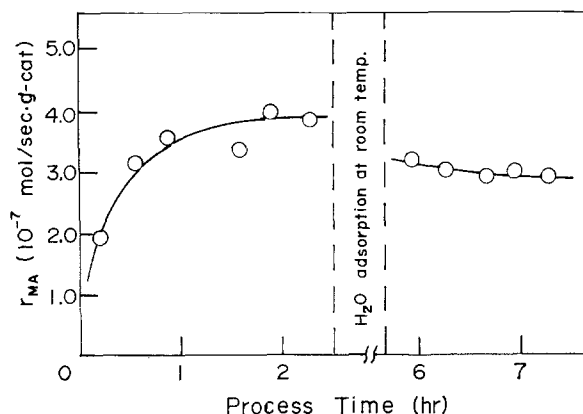


FIG. 8. Effect of H₂O addition on carbonylation activity on Rh-Y. Reaction conditions are the same as shown in Fig. 2.

the amount of residual rhodium was more than the lost rhodium. The deactivation process shown in Fig. 4, therefore, is not interpreted only by the loss of rhodium species from the catalyst system. From X-ray diffraction measurements, it was found that the zeolite framework with a high content Rh-Y was decomposed more easily than that with a low content Rh-Y. The deactivation process was also caused by the decomposition of the zeolite framework. It is suggested that the active site consists of a rhodium species anchored firmly in the zeolite framework by a cation exchange process and located rather large distances from other sites, i.e., about 2 rhodium sites per unit cell.

It has been shown that Rh cation is reduced to zero-valent Rh when Rh-Y is calcined in He or H₂ at temperatures higher than 573 K (10). When Rh-Y was calcined at 573 K in He or H₂, the catalytic activity was very sharply reduced. On the other hand, Rh-Y catalyst treated in the usual way showed an induction period, which disappeared when the catalyst was calcined at 473 K in He for 2 hr. Moreover, when the Rh-Y calcined at 473 K was exposed to water vapor at room temperature, the induction period reappeared as shown in Fig. 5. These results suggest

that the active site does not consist of zero-valent rhodium and that a trivalent rhodium species is the precursor of the active site. If the feed of reactants was stopped when the reaction rate has reached a steady state, and then the catalyst was exposed to water vapor at room temperature prior to starting the reaction again under the same reaction conditions, the induction period was not observed as shown in Fig. 8. So, it is suggested that water molecules adsorbed in the zeolite reduce the rate at which the active site is formed from trivalent rhodium, but do not poison the active site once it is formed.

The active site for Rh-Y was irreversibly deactivated by reactions at temperatures higher than 473 K, while on the other hand, in the Rh-X zeolite catalyst, the optimum reaction temperature range was reported to be 503–523 K (14, 15). The activity of our Rh-Y zeolite catalyst decreased considerably above 473 K. These two zeolite catalysts were prepared under different conditions, such as the pH value of the ion exchange solution. However, it is not clear that the difference between the thermal stabilities of these catalysts was caused by the difference between their preparation conditions, or the kinds of zeolite.

CONCLUSION

(i) Rh-Y zeolite catalyst shows a high activity for the carbonylation of methanol in the presence of methyl iodide at 423–473 K under atmospheric pressure. The main product in this reaction is methyl acetate although the formation of acetic acid increases with contact time. These results suggest that the rhodium complex catalyst could be successfully heterogenized by using zeolite.

(ii) The precursor of the active site is a trivalent rhodium which is firmly anchored on the zeolite by a cation exchange process. The water adsorbed in the zeolite prevents the formation of the active rhodium site.

(iii) The active rhodium sites on the Y zeolite are stable up to 473 K, but are irreversibly deactivated at temperatures over 473 K.

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