JOURNAL OF CATALYSIS 69, 498–501 (1981)

# Infrared Study of the Rh–X Zeolite Catalyst in the Carbonylation of Methanol

## INTRODUCTION

A large fraction of acetic acid produced today is based on methanol carbonylation using the low-pressure, rhodium-and-iodide liquid-phase process developed by Monsanto (*1*), the catalytic cycle of which involves rhodium complexes (*2*). Nefedov *et al.* (*3, 4*) used a rhodium-exchanged zeolite (RhNaX) catalyst to carbonylate methanol in the vapor phase and found the reaction to proceed at atmospheric pressure with good selectivity. Scurrell (*5*) obtained limited ir spectra of a RhNaX pellet after exposure to CO and $CH_3I$ which showed carbonyl and acetyl frequencies, while Takahashi *et al.* (*6*) found the vapor-phase carbonylation of methanol catalyzed by RhNaY to have the same kinetics as the liquid-phase homogeneous reaction.

The objectives of the present work were to study self-supporting wafers of RhNaX by infrared spectroscopy after *in situ* treatments of the wafers with CO, $CH_3OH$, and $CH_3I$, individually or in mixtures, under static or flow conditions and, thus, to obtain evidence about rhodium-complex formation in the methanol carbonylation environment.

## EXPERIMENTAL

Molecular sieve 13X, purchased in powder form from the Linde Division of the Union Carbide Corporation, was used after subjection to size fractionation for obtaining submicron particles for making transparent self-supporting wafers.

Rhodium trichloride trihydrate was used for preparing 3 wt% Rh zeolite by ion exchange. Analysis of both the ion exchange filtrate and the dried, exchanged zeolite showed that each rhodium ion replaced three sodium ions in the zeolite.

Self-supporting disks of rhodium-exchanged zeolite were made using a 13-mm KBr die and pressing a mass of about 15 mg of zeolite to a pressure of 34 MPa. The disks were placed in a heated and evacuable infrared cell made of stainless steel and fitted with NaCl windows. The cell was connected either to a vacuum manifold for exposing the zeolite to known subatmospheric pressures of reactants, individually or in mixtures, under static conditions or to a flow system for exposing the zeolite to reactants under continuous flow conditions. When flow conditions were used a matched cell was placed in the reference beam of the spectrometer in order to subtract the spectra of the gaseous phase. Spectra of the disks were recorded at cell temperatures of 323 or 423 K using a Perkin–Elmer model 283 spectrophotometer.

## RESULTS AND DISCUSSION

The infrared spectrum of the dehydrated (evacuating to about 0.1 Pa and stepwise heating of the cell to 873 K) zeolite disk is shown in Fig. 1A where the band at 1650 $cm^{-1}$ is due to physically adsorbed water molecules. Subsequent contact of the catalyst with 53 kPa of CO at 323 K for 30 min gave rise to spectrum 1B, recorded in the presence of the gas phase. The band at 2166 $cm^{-1}$ and the shoulder of the 2085-$cm^{-1}$ band are due to the ir absorption of CO in

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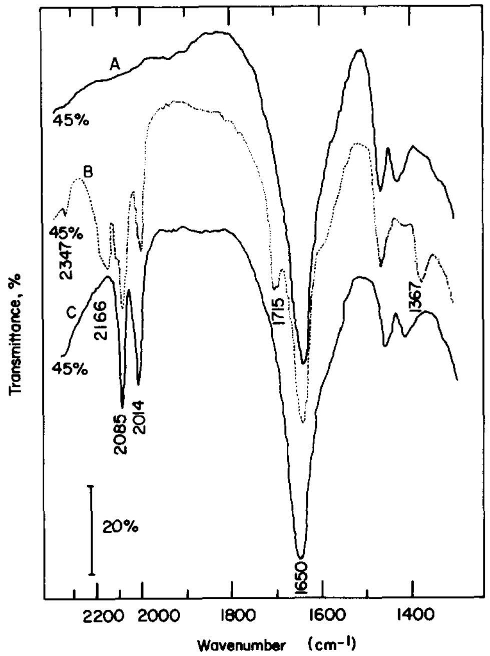

FIG. 1. Infrared spectra of RhNaX during adsorption of CO at 323 K: (A) Background spectrum; (B) after adsorption of CO in the presence of the gas phase; (C) after adsorption and evacuation of the gas phase.

the gas phase. The band at 2347 $cm^{-1}$ has been assigned (*7*) to the antisymmetric linear vibration of physically adsorbed carbon dioxide molecule, while the bands at 1715 and 1367 $cm^{-1}$ have been assigned to chemisorbed $CO_2$. Thus, the bands at 2085 and 2014 $cm^{-1}$ must be due to Rh–carbonyl species. Further, exposure of the wafer to CO at 323 K and subsequent evacuation for 10 min gave rise to spectrum 1C, which shows that the $CO_2$ bands disappear upon evacuation and that the 2085- and 2014-$cm^{-1}$ bands ultimately become equally strong.

Figure 2 shows spectra of the zeolite wafer with Rh–carbonyl species already formed (A) after various vacuum heat treatment stages (B–E). These spectra show that the relative intensities of the 2085- and 2014-$cm^{-1}$ bands remain invariant during these treatments, and this implies that the carbonyl bands are due to a single specie, i.e., a Rh–dicarbonyl specie. The presence of $CO_2$ bands, Fig. 1B, during the initial exposure of the wafer to CO provides strong evidence that, in analogy with the homogeneous phase reduction of Rh(III) to Rh(I) by CO (*8*), i.e.

$$Rh^{III} - H_2O + 3CO \rightarrow Rh^{I}(CO)_2 + CO_2 + 2H^+, \quad (1)$$

the Rh(III) ions in the zeolite are reduced to Rh(I), and that the dicarbonyl specie formed is a Rh(I)–dicarbonyl (A′) specie with carbonyl frequencies at 2085 and 2014 $cm^{-1}$. These frequencies are similar but higher than the 2064- and 1989-$cm^{-1}$ bands of $[Rh^{I}(CO)_2I_2]^-$ (*2*), the differences arising from ligand differences. The equal intensity of the bands of (A′) imply that the angle between the C–O bond directions is 90°.

The varying relative intensities of the 2085- and 2014-$cm^{-1}$ bands, Fig. 1B, during the CO treatment must be due to the simultaneous presence of Rh(III) and Rh(I) carbonyls. Indeed, the reduction of hydrated Rh(III) ions and other metals by CO has

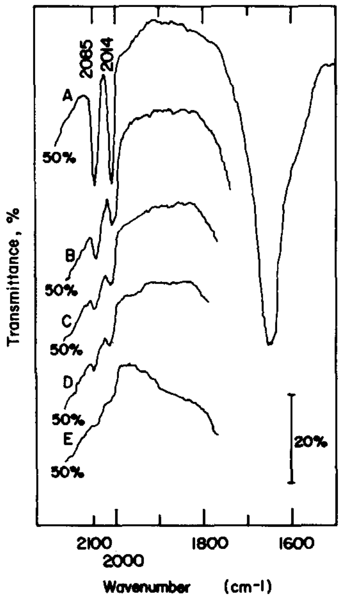

FIG. 2. Spectra of RhNaX after exposure to CO: (A) Evacuated at 323 K for 10 min; (B) evacuated at 473 K for 2 hr 45 min; (C) continuously evacuated at 673 K for 15 min; (D) evacuated at 673 K for 10 min more; and (E) evacuated at 723 K for 20 min.

been postulated (*8–10*) to proceed via a CO-insertion reaction as the rate-determining step. With the CO-insertion reaction as the slow step, the coexistence of $Rh^{III}$–CO and $Rh^{I}(CO)_2$ species with overlapping frequencies at 2085 $cm^{-1}$ is very plausible, and this coexistence would account for the relative intensity variation of the 2085- and 2014-$cm^{-1}$ bands during the reduction stage.

Following the formation of the above-described complex, the disk was exposed to 40 kPa of $CH_3I$ at 323 K for 1 hr and then the cell was evacuated for 5 min before recording the spectrum. The spectrum, Fig. 3A, shows that the carbonyl stretching modes at 2085 and 2014 $cm^{-1}$ were replaced by strong bands at 2076 and 1720 $cm^{-1}$. The 2076-$cm^{-1}$ peak can be inferred to be a carbonyl frequency and the peak at 1720 $cm^{-1}$ an acetyl one. The 1720-$cm^{-1}$ band cannot be due to adsorbed acetic acid because spectra (*11*) of zeolite doped with acetic acid show an additional very strong band at 1589 $cm^{-1}$ which has been assigned (*12*) to adsorbed acetate ion, i.e., vibration of the $COO^-$ group, and this band is practically absent from spectrum 3A. The 1720-$cm^{-1}$ band cannot be due to methyl acetate either because evacuation of the cell at 323 K would have removed it. Therefore it must be concluded that the 1720-$cm^{-1}$ band is due to an acetyl group bound to the rhodium species, and that, in analogy with the homogeneous phase system, methyl iodide oxidatively adds to the previously formed Rh(I)–dicarbonyl complex yielding, after migration of the methyl group, a Rh(III)–specie (C′) with one carbonyl and one acetyl group. Spectra B–E of Fig. 3 recorded after various heat treatments show that the Rh–acyl complex formed by the aforementioned treatment is also a rather stable specie.

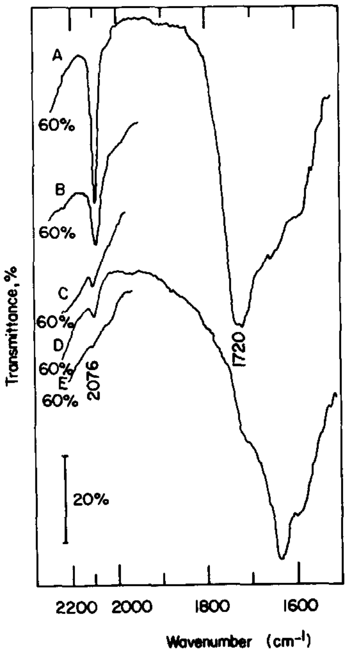

FIG. 3. Spectra of RhNaX after sequential exposures to CO and $CH_3I$: (A) Evacuated at 323 K for 5 min; (B) evacuated at 373 K for 2 hr; (C) evacuated at 600 K for 15 min; (D) evacuated at 603 K for 20 min; (E) evacuated at 633 K for 8 min.

In order to obtain spectra under reaction conditions, the RhNaX pellet (dehydrated using a nitrogen gas stream at 573 K for 10 hr) was exposed to a mixture of CO, $CH_3I$, and $CH_3OH$ under continuous flow conditions at 423 K and spectra were recorded continuously. Gas chromatographic analysis of the condensed effluent stream showed the presence of methyl acetate, water, and dimethyl ether but no acetic acid, which may, however, have been present in a quantity too small to be detected. Figure 4 gives a typical spectrum which shows bands at 2141, 2065, 1995, 1722, and 1589 $cm^{-1}$. The 1589-$cm^{-1}$ peak is due to adsorbed acetate ions which implies that some acetic acid was formed. The presence of the other bands implies that more than one rhodium complex species are present simultaneously under reaction conditions (continuous feed of reactants and promoters). The very strong 1722 $cm^{-1}$ band may be due to all the possible rhodium–acyl complexes as well as to the carbonyl frequency of adsorbed acetic acid. The 1995-$cm^{-1}$ frequency is very close to the 1989-$cm^{-1}$ antisymmetric carbonyl fre-

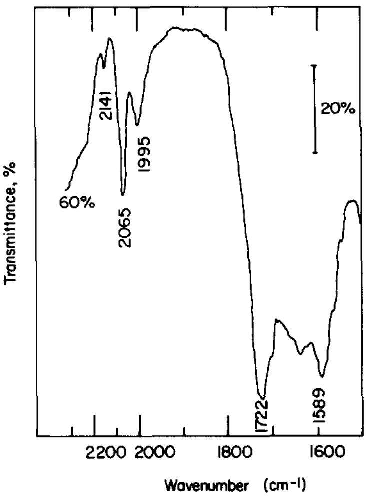

FIG. 4. Infrared spectrum of RhNaX after exposure to CO–$CH_3OH$–$CH_3I$ mixture under continuous flow conditions at 423 K.

quency of $[Rh(CO)_2I_2]^-$ (*2*), while the 2065-$cm^{-1}$ one is identical to the 2064-$cm^{-1}$ symmetric carbonyl band of the same anionic specie. On the basis of this spectrum and the spectral information presented previously, it must be concluded that Rh(I)–dicarbonyl species are present on the zeolite. However, the unequal intensities of the 2065- and 1995-$cm^{-1}$ bands indicate that the 2065-$cm^{-1}$ band probably arises partly from the Rh(I)–dicarbonyl complex and partly from other complexes, possibly $[Rh(CO)L_4]$, the carbonyl frequency of the latter being 2070 $cm^{-1}$ (*13*). The 2141-$cm^{-1}$ band may be due to physically adsorbed CO and/or rhodium–carbonyl species. This spectrum shows that the carbonyl frequencies of the Rh(I)–dicarbonyl specie formed under flow conditions are much closer to the frequencies of the species formed from the homogeneous phase, and this means that a carbonyl–iodo–rhodium specie is formed under reaction conditions.

In summary, the spectra of this study show that, in the carbonylation of methanol in the presence of rhodium-exchanged zeolites, the Rh(III) ions are reduced to Rh(I) ions which lead to rhodium–dicarbonyl and rhodium–carbonyl–acetyl complexes which are involved in the catalytic cycle of the above reaction system. These data, then, provide further confirming evidence that the above cycle is similar to that of the homogeneous phase system.

## ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant ENG 77-20678 and by the Petroleum Research Fund, administered by the American Chemical Society.

The authors wish to extend their thanks to Dr. P. Fanwick of the University of Kentucky for very helpful discussions.

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*Received May 6, 1980; revised December 22, 1980*

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