

Carbonylation of Benzene in a Zeolite Catalyst

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The application of zeolites as acid catalysts in the production of specialty chemicals has significant commercial importance. The broad range of electrophilic agents that react with aromatic compounds in zeolites provide many potentially useful products.¹ It has been shown recently that CO and H₂O can react with small alkenes in the zeolite H-ZSM-5 to form carboxylic acids.² Under the same conditions but in the absence of water, it was also shown that ethene, isobutene, and 1-octene react to form ketones instead of carboxylic acids.³ Under more strongly acidic conditions such as in the presence of HCl/AlCl₃, CO reacts directly with aromatics such as benzene.^{4,5} In this paper, we demonstrate the formation of benzoic acid in the zeolite H-Y and benzaldehyde in AlCl₃-doped H-Y from the direct reaction of benzene and CO.⁶

Carbonylation of benzene with carbon monoxide is known to require the presence of Lewis and Brønsted acids.^{4,5} Steamed zeolites are widely believed to have both Brønsted and Lewis acid sites. Furthermore, cooperative effects between Brønsted and Lewis acid sites in zeolite catalysts have been discussed for some time.^{7–9} As an example, activity in alkane cracking reactions can be enhanced by a factor of 5 or more in H-Y that has been dealuminated with steam versus ammonium hexafluorosilicate. The H-Y sample used in this study, denoted PQ(7), has been characterized previously⁹ and was shown to exhibit this type of activity enhancement, suggesting that this sample might be active as a carbonylation catalyst.

Samples for NMR¹⁰ were prepared by placing 50–100 mg of the PQ(7) sample into glass sample tubes and evacuating to a pressure of less than 1.0×10^{-5} Torr at 750 K for 12 h. After being cooled to liquid nitrogen temperature, samples were dosed with controlled volumes of benzene and to various pressures of ¹³C-labeled carbon monoxide. Samples were sealed in glass tubes and allowed to stand at room temperature for varying lengths of time or were heated prior to being transferred to NMR rotors under an inert atmosphere. Zeolite samples containing pure carbonyl-¹³C-labeled benzaldehyde for comparison were prepared following a similar procedure.

The data shown in Figure 1 were obtained following adsorption of benzene and CO on pure PQ(7). The spectrum shown in Figure 1a is the result of exposure of the zeolite to 1000 μmol/g of pure, unenriched benzene. A single, isolated feature is observed at 129.4 ppm from TMS, similar to pure liquid benzene at 128.5 ppm. The 0.9-ppm shift in the resonance frequency is due to introduction of the benzene molecule into the environment of the zeolite cavity.¹¹ Figure 1b shows the results obtained after exposure of the zeolite sample to 1000 μmol/g of benzene, followed by exposure to 200 Torr of carbon monoxide. The sample was allowed to stand at room temperature for 24 h prior to transfer to the NMR rotor. The only signal observed after this treatment corresponds to unreacted benzene, 129.5 ppm.

The system shows new features at 178.2 and 186.0 ppm on heating to 110 °C, Figure 1c, or on heating to 150 °C, Figure 1d. These features are most likely due to the formation of benzoic acid, as in ref 2. Even though the H-Y samples were thoroughly outgassed under high vacuum at high temperature, we cannot rule out the presence of trace amounts of water which would lead to the formation of benzoic acid and account for the observed features. One cannot interpret these features as being due to benzene¹² since we do not observe signal at these frequencies for the case of pure benzene, as shown Figure 1a. Carbon monoxide, either chemisorbed or freely translating in the zeolite pores, is another possibility.¹³ However, we do not observe signal on exposure of the zeolite to pure CO, Figure 1e, probably due to desorption during sample transfer.

The results of the coadsorption experiment were different when the PQ(7) sample was doped with AlCl₃. Catalyst samples were prepared by using a variation of published procedures,¹⁴ by transferring a small amount of AlCl₃ into a Teflon autoclave liner under an inert atmosphere. A small amount of degassed zeolite was placed into a 5-mL Pyrex beaker, which was then placed into the autoclave liner. The autoclave was then sealed and heated in a convection oven at 150 °C for 90 min. After being cooled to room temperature, a portion of the zeolite was reintroduced to the vacuum manifold, and then evacuated to the background pressure at room temperature. This sample was then exposed to benzene and CO, as discussed above.

Figure 2a shows the spectrum obtained after exposure of the AlCl₃-promoted PQ(7) to 1000 μmol/g of benzene, followed by exposure to 400 Torr of carbon monoxide. The spectrum shows a feature at 129.3 ppm, due to pure unreacted benzene, as well as a feature at 205.4 ppm, due to the formation of benzaldehyde. The spectrum also shows spinning sidebands at 265.3, 145.3, and 85.3 ppm, consistent with the magic angle spinning frequency of 3015 Hz. Finally, Figure 2b is the result obtained after exposure of the PQ(7) sample to pure benzaldehyde. The feature at 205.5 ppm is due to the carbonyl carbon in benzaldehyde, and spinning sidebands at 265.5 and 146.7 ppm are observed as distinct features.

The assignment of the feature at 205.4 ppm in Figure 2a as benzaldehyde is supported by results from several previous investigations in addition to the data shown here. First, Olah and co-workers observed the chemical shift of benzaldehyde in magic acid solutions as 205.9 ppm.¹⁵ Second, we observed sites in steamed H-Y which are capable of polarizing the carbonyl group in acetone to nearly the same extent as magic

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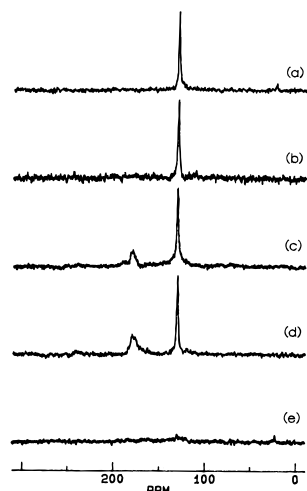


Figure 1. Undoped H-Y with the following: (a) 1000 $\mu\text{mol/g}$ of benzene with the sample held at room temperature for 19 days (32768 scans; MAS frequency 3017 ± 10 Hz), (b) 1000 $\mu\text{mol/g}$ of benzene and 200 Torr of CO with the sample held at room temperature for 1 day (16384 scans, MAS frequency 4049 ± 10 Hz), (c) 1000 $\mu\text{mol/g}$ of benzene and 200 Torr of CO with the sample held at 110 $^{\circ}\text{C}$ for 4 h and at room temperature for 5 days (34934 scans, MAS frequency 3004 ± 10 Hz), (d) 1000 $\mu\text{mol/g}$ of benzene and 457 Torr of CO with the sample held at 150 $^{\circ}\text{C}$ for four 7-h periods over 8 days (32768 scans, MAS frequency 3017 ± 3 Hz), and (e) 200 Torr of CO with the sample held at room temperature for 11 days (32768 scans, MAS frequency 3017 ± 10 Hz).

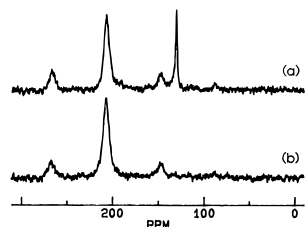
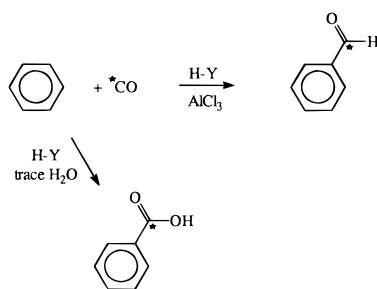


Figure 2. (a) AlCl_3 -promoted H-Y with 1000 $\mu\text{mol/g}$ of benzene and 404 Torr of CO. The sample was held at room temperature for 9 days (16384 scans, MAS frequency 3014 ± 10 Hz). (b) Undoped H-Y with 210 $\mu\text{mol/g}$ of pure ^{13}C -carbonyl-labeled benzaldehyde (16384 scans, MAS frequency 3020 ± 10 Hz).

Scheme 1



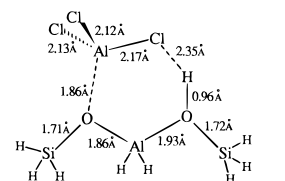
acids.¹⁶ Also, by examining pure AlCl_3 , Nicholas and co-workers have characterized several carbocation structures and found the chemical shifts to be nearly identical with those seen in magic acid solution.¹⁷

Scheme 1 illustrates the different pathways that are available for the reaction of benzene with carbon monoxide and how the reaction pathway depends upon the type of acid sites present in the zeolite. The formation of benzoic acid seems to be

favorable in the AlCl_3 -free zeolite, while the presence of AlCl_3 promotes the formation of benzaldehyde. Both pathways can be explained by the formation of an acylium cation via initial protonation of benzene.³ Another possibility is the formation of a formyl cation from CO,⁵ followed by direct electrophilic attack on benzene by the formyl cation to form a benzenium ion. The NMR data shown here cannot distinguish between these two processes.

Additional insight into the first step in the reaction mechanism can be obtained from an examination of the relative gas-phase proton affinities of benzene and CO. In zeolites, this approach has proved to be useful for scaling the relative energies of reaction intermediates and for predicting the favorable reaction pathway when multiple pathways are possible.¹⁸ The gas-phase proton affinity of benzene is somewhat higher than that of CO, 185.8 vs 139.0 kcal/mol.¹⁹ This suggests that the first step in the reaction should probably be viewed as the formation of a benzenium ion, although this interpretation clearly depends on the nature of the active site.

We are currently examining the active sites in the Lewis acid-promoted zeolites using a variety of techniques based on incorporation of carefully controlled amounts of metal halides into the zeolite. Using thermogravimetric analysis to measure the weight uptake, we have currently been able to form stoichiometric, 1:1 adsorption complexes of BCl_3 , AlCl_3 , and SbF_5 at the Brönsted sites in the zeolite H-ZSM-5. These data, along with preliminary computations and NMR data, suggest that we are observing a tetrahedral complex at the Brönsted site, **1**,²⁰ similar to that reported by Markova and coworkers.²¹



It is possible that this complex is the active site in the carbonylation reaction. We also note that the 1:1 complexes are stable above 700 K, depending on the specific zeolite and Lewis acid combination and pretreatment conditions. This suggests that variations of these materials might be useful as heterogeneous catalysts.

Finally, we recognize that trace amounts of water can react with AlCl_3 to produce HCl gas, which can then react with an additional AlCl_3 to form HAlCl_4 .⁴ This would still allow the reaction to proceed, but would not involve participation of the zeolite Brönsted sites. Under these conditions, the system may be thought of as a high-surface area form of AlCl_3 with the zeolite as a support. However, comparison of the signal-to-noise ratios in Figure 2, parts a and b, suggests that 200 $\mu\text{mol/g}$ of benzaldehyde is forming, and this cannot all be accounted for by the presence of trace amounts of water. As discussed above, further experiments are in progress to resolve this issue.

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