

¹³C NMR Study of the Carbonylation of Benzene with CO in Sulfated Zirconia

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Friedel–Crafts acylation¹ of butene and ethene to form ketones in the solid acid zeolite H-ZSM-5 at 296 K has recently been reported.² An earlier study demonstrated that small olefins are converted to carboxylic acids (the Koch reaction³) in the presence of CO and water in H-ZSM-5 at 296 K.⁴ The carbonylation of aromatic hydrocarbons with CO is also feasible,^{5–7} although requiring more highly acidic conditions. Addition of metal–halide Lewis acids to enhance the Brønsted acidity⁸ of the zeolite H–Y allows the carbonylation of benzene with CO to proceed readily.⁹ Another promising family of materials are the sulfated zirconias.¹⁰ These materials are known to catalyze the isomerization of small alkanes at relatively low temperature,¹⁰ although the exact mechanism for this may involve trace alkene impurities.¹¹ The use of metal-promoted sulfated zirconia as a catalyst in the carbonylation of aromatics with CO has recently been reported,⁷ although pure sulfated zirconia was reportedly not active in the reaction. The present paper extends the previous work^{2,3,7} to include a direct spectroscopic measurement of the carbonylation of benzene with CO, the Gattermann–Koch reaction,⁵ using sulfated zirconia as the solid acid catalyst.

Sulfate-doped zirconia and pure zirconia samples were obtained from Magnesium Electron, Inc. (XZ0682.01 and XZ0632.03, respectively). The sulfate-doped and pure zirconia samples were pretreated by heating to 600 °C for 1 h in flowing dry O₂. The number of Brønsted acid sites in each material was determined with thermogravimetric analysis (TGA) of isopropylamine from the number of amine molecules which desorb between 575 and 650 K.^{12,13} The sulfated zirconia sample had a site concentration of 80 μmol/g. While the number of Brønsted sites is known to depend strongly on pretreatment conditions,¹⁴ we observe a significant difference between the sulfated zirconia and the pure zirconia, which had a site concentration of <10 μmol/g and was inactive in the carbonylation reaction.

The chemistry of benzene and CO in sulfated zirconia was studied with ¹H–¹³C cross-polarization magic angle spinning

(CPMAS) NMR spectroscopy.¹⁵ Samples were weighed, placed in shallow beds in one-half inch horizontal glass tubes on a vacuum manifold, and outgassed at 700 K until the pressure returned to the background value of less than 1.0 × 10^{–5} Torr, ~6 h. After the samples were cooled to liquid nitrogen temperature, some samples were dosed with controlled volumes of unlabeled benzene and controlled pressures of ¹³C-labeled carbon monoxide (Cambridge Isotopes Labs). Other samples were cooled to room temperature and were dosed with controlled volumes of carbonyl ¹³C-labeled benzaldehyde or benzoic acid (Cambridge Isotopes Labs). The samples were sealed in glass tubes and kept in liquid nitrogen until being warmed to room temperature and transferred to NMR rotors under an inert atmosphere.

Figure 1a is the result obtained after adsorption of benzene and ¹³C-labeled carbon monoxide to sulfated zirconia and warming to room temperature for 5 days inside the sealed glass tube. The figure shows the presence of spectral features at 206 and 176 ppm (from TMS) that we interpret as being due to the formation of benzaldehyde and benzoic acid, respectively. A possible mechanism of the reaction is outlined in Scheme 1. We speculate that the acylium cation **1** is formed as an intermediate,^{2,16} although it is not observed in the NMR spectrum. Upon undergoing a hydride shift and loss of a proton, **1** is converted to benzaldehyde **2**. Oxidation of benzaldehyde produces benzoic acid **3**. This is not surprising when one considers earlier studies in which the redox properties of the sulfated zirconia were examined.^{17,18} Carbon monoxide¹⁹ is not observed in these experiments, probably due to desorption during the transfer of the samples to the NMR rotors. The feature at 130 ppm is the natural abundance signal due to unreacted benzene. We also note here that the pure zirconia sample did not produce the reaction product features under the conditions of this experiment.

The assignment of the product features as benzaldehyde and benzoic acid is substantiated with the results shown in Figure 1b–d. Figure 1b was obtained after adsorption of benzaldehyde to the sulfated zirconia sample at a coverage of 0.38 molecules per Brønsted site. This spectrum shows a single feature centered at 206 ppm from TMS, with spinning sidebands at 126 and 286 ppm. Identical features are observed in the spectrum obtained at 0.70 molecules per site (Figure 1c). The observed isotropic chemical shift of 206 ppm is very close to values obtained for benzaldehyde in magic acid (205.7 ppm),²⁰ while the carbonyl resonance for benzaldehyde in CDCl₃ solution is 192.15 ppm.²¹ This suggests that the carbonyl carbon in the benzaldehyde molecule has been substantially deshielded by interactions with the environment, analogous to those observed in zeolites^{22–25}

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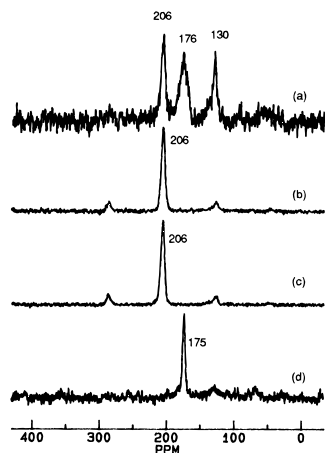
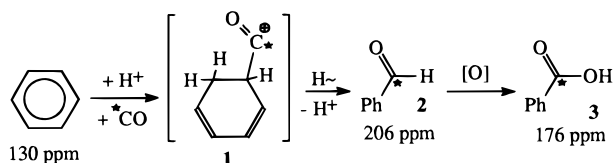


Figure 1. CPMAS spectrum of sulfated zirconia exposed to (a) 79 $\mu\text{mol/g}$ of benzene and 452 Torr of $^{13}\text{C}^{18}\text{O}$; (b) 0.38 molecules/site of $\text{C}_6\text{H}_5^{13}\text{CHO}$, 32 768 scans; (c) 0.70 molecules/site of $\text{C}_6\text{H}_5^{13}\text{CHO}$; and (d) 0.40 molecules/site of $\text{C}_6\text{H}_5^{13}\text{CO}_2\text{H}$.

Scheme 1



and liquid acids.²⁶ The spectrum does not change with time, suggesting that the benzaldehyde molecule is adsorbed as a stable complex at the Brønsted site. Figure 1d is the result obtained after exposure of the sulfated zirconia sample to benzoic acid at a coverage of 0.44 molecules per Brønsted site. We observe a carbonyl feature at 175 ppm as well as a smaller feature at 130 ppm due to aromatic carbons. The chemical shift of the carbonyl carbon in benzoic acid is 172.61 in CDCl_3 solution.²¹

The Brønsted site appears to play a special role in stabilizing the benzaldehyde molecule on the surface of the sulfated zirconia. When pure zirconia is exposed to benzaldehyde, we obtain significantly different results, shown in Figure 2, than we obtained for the sulfated zirconia samples. In the absence of these sites, benzaldehyde reacts rapidly to form benzyl benzoate (Scheme 2). Figure 2a shows the results obtained after exposure of the pure zirconia sample to benzaldehyde and immediate insertion into the NMR spectrometer. The prominent features in the spectrum can be seen clearly after ~ 200 scans. We interpret the resonances at 204 and 104 ppm as being due to the formation of an acetal-like intermediate **4** and the resonances at 175 and 73 ppm as being due to benzyl benzoate **5**. The chemical shifts of the labeled positions in **4** are consistent with those in similar aromatic acetals, all of which have ester carbons with resonances in the range of 102–105 ppm in CDCl_3 solution.²¹ In our interpretation, benzaldehyde is either not observed due to rapid reaction or is seen as an overlapping resonance at 204 ppm.

We confirmed the formation of benzyl benzoate with two additional experiments. First, we examined the time progression of the reaction. The features at 204 and 104 ppm disappear with time with respect to the features at 175 and 73 ppm, as

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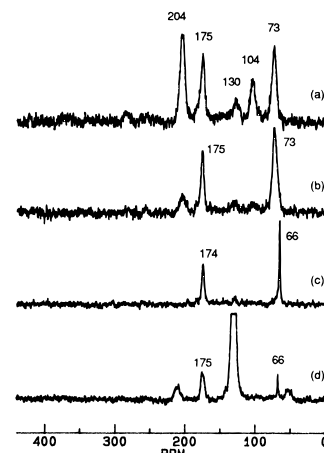
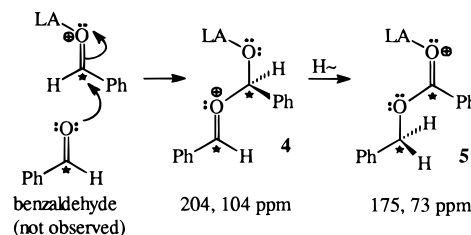


Figure 2. CPMAS spectrum of zirconia exposed to 32 $\mu\text{mol/g}$ of $\text{C}_6\text{H}_5^{13}\text{CHO}$, with acquisition initiated (a) on insertion of sample into spectrometer, (b) 48 h after sample insertion, and (c) 72 h after sample insertion, sample exposed to room air; (d) 50 $\mu\text{mol/g}$ of unlabeled benzyl benzoate on pure zirconia, sample exposed to room air.

Scheme 2



seen in Figure 2b, taken 48 h after the sample was warmed to room temperature. Figure 2c was obtained after 72 h, with the sample equilibrated in room air for ~ 24 h. The observed resonances are sharpened and shifted slightly to 174 and 66 ppm, probably due to adsorption of water and displacement of the molecule from the Lewis acid sites on the surface of the solid. Second, we compared the reaction products with adsorbed benzyl benzoate. Figure 2d is the spectrum obtained after exposure of the pure zirconia sample to unlabeled benzyl benzoate in room air. We observe well-defined resonances at 175 and 66 ppm, as well as a large feature with side bands centered at 130 ppm due to aromatic carbon atoms. The correspondence of the peaks at 175 and 66 ppm with the product features in Figure 2c supports the assignment of the product as benzyl benzoate.

We note here that zirconia and alumina both catalyze the dimerization reaction of benzaldehyde to benzyl benzoate at room temperature. In a separate experiment, we confirmed this by adsorbing benzaldehyde on alumina. The spectra that were obtained are indistinguishable from those shown in Figure 2a–c. In similar studies of acetone in alumina, it was shown that rapid condensation to form mesityl oxide and higher condensates occurs rapidly at room temperature^{27,28} via an enol intermediate. An important difference between the previously reported reactions and those observed in the present study is that benzaldehyde does not have an enol, suggesting the different mechanism shown in Scheme 2 which apparently involves a hydride shift.

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