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NMR Observation of the Koch Reaction in Zeolite H-ZSM-5 under Mild Conditions

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Since the work of Koch published in 1955, it has been known that carboxylic acids can be produced in high yields by the action of carbon monoxide on alcohols or CO and H_2O on olefins in concentrated mineral acids (typically sulfuric acid) under moderate temperature and pressure conditions (253−353 K, <100 bar) (the Koch reaction).[1] If formic acid is used as the source of CO, the reaction proceeds in H_2SO_4 medium at 273−313 K and atmospheric pressure to produce mainly tertiary carboxylic acid (the Koch−Haaf reaction).[2]

In industrial applications of the Koch reaction, one of the major problems is the presence of huge amounts of a mineral acid in the waste. A possible solution may be to use solid acids as catalysts instead of liquid mineral acids. In 1984, carbonylation of methanol into methyl acetate, methyl formate, and acetic acid was reported on solid acids.[3] But the reaction proceeded only at elevated temperature and pressure (473−573 K, 10 bar) and had either a very low yield (0.3%) under 100% selectivity or a low selectivity (0.8%) under 34.6% yield, the formation of dimethyl ether being the main non-carbonylating route of the reaction. In 1987, carbonylation of olefins into corresponding acids on modified pentasyl-type zeolites with a yield near 50% was reported, but it again proceeded only at high temperature and pressure; for pure acidic forms of zeolites, the reaction conditions were around 573 K and 300 bar.[4]

We report here on an NMR observation of the Koch reaction in zeolite H-ZSM-5 catalyst at room temperature without application of pressurized conditions. We have found that *tert*-butyl alcohol (*t*-BuOH) or isobutylene (*i*-C_4H_8) is selectively transformed into trimethylacetic acid at 296 K with high yield (50% for *t*-BuOH and 85% for *i*-C_4H_8[5]) after coadsorption of the alcohol and CO or olefin, CO, and water on H-ZSM-5.

A well-characterized H-ZSM-5 zeolite sample (Si/Al=49)[6] was activated by heating at 450 °C under vacuum (10^{-5} Torr) for 4 h. We then froze out equal amounts of *t*-BuOH and CO (or *i*-C_4H_8, CO, and H_2O) on H-ZSM-5 under vacuum at the temperature of liquid nitrogen, and the glass tube with the zeolite was sealed off from the vacuum system. Further, the sample was slowly warmed to room temperature and kept at 296 K for a few hours. The reaction products were analyzed directly inside the zeolite with ^{13}C CP/MAS NMR.[7] Additionally, we dissolved the zeolite framework and then analyzed the liberated organic products with GC-MS.

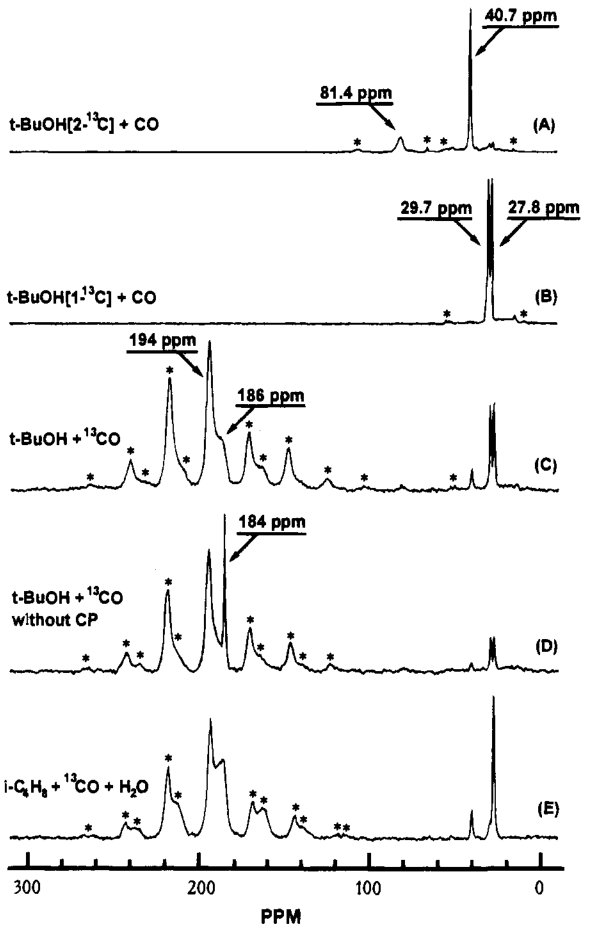

Figure 1. ^{13}C CP/MAS NMR spectra for the products formed after coadsorption of *t*-BuOH and CO or *i*-C_4H_8 , CO, and H_2O on H-ZSM-5 zeolite. (A) Coadsorption of the *t*-BuOH, ^{13}C-labeled in the quaternary carbon atom (82% ^{13}C enrichment), and unlabeled CO. (B) Coadsorption of the *t*-BuOH, labeled with ^{13}C in a methyl group (67% ^{13}C enrichment), and unlabeled CO. (C) Coadsorption of the ^{13}C-labeled CO (90% ^{13}C enrichment) and unlabeled *t*-BuOH. (D) One pulse excitation spectrum with high-power proton decoupling, recorded after coadsorption of the ^{13}CO and unlabeled *t*-BuOH. This spectrum corresponds to spectrum C but was recorded without cross-polarization. (E) Coadsorption of the unlabeled isobutylene, ^{13}C-labeled CO (90% ^{13}C enrichment), and water. In each case, 300 μmol/g of *t*-BuOH and CO or *i*-C_4H_8 , CO, and H_2O was adsorbed; 6000 scans have been collected for (A), 3000 scans for (B), 16000 scans for (C), 2200 scans for (D), 20000 scans for (E). Asterisks denote spinning side bands.

^{13}C CP/MAS NMR spectra recorded after coadsorption of *t*-BuOH and CO or *i*-C_4H_8, CO, and H_2O on H-ZSM-5 are given in Figure 1. When taken together, these spectra can easily be rationalized in terms of formation of trimethylacetic acid (TMAA) as the main reaction product. Indeed, if we use for coadsorption *t*-BuOH-2-^{13}*C*, i.e., the alcohol labeled in the quaternary carbon atom, and unlabeled CO, then two signals at 40.7 and 81.4 ppm dominate (Figure 1A). The appearance of

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[1] (a) Koch, H. *Brennstoff-Chemie* **1955**, *36*, 321−328. (b) For a review, see: Bahrmann, H. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer Verlag: Berlin, 1980; pp 372−413.

[2] (a) Koch, H.; Haaf, W. *Angew. Chem.* **1958**, *70*, 311. (b) Koch, H.; Haaf, W. *Org. Synth.* **1964**, *44*, 1.

[3] Fujimoto, K.; Shikada, T.; Omata, K.; Tominaga, H. *Chem. Lett.* **1984**, 2047−2050.

[4] Hoelderich, W.; Reuvers, J.; Kummer, R.; Hupfer, L. Eur. Pat. 249 976, Dec 23, 1987.

[5] The percentage alcohol or olefin conversion into trimethylacetic acid was estimated from the intensities of the corresponding signals of the methyl groups in one-pulse-excitation ^{13}C MAS NMR spectra, recorded without cross-polarization (see Figure 1D) and with the repetition time during accumulation of the NMR spectra equal to $10T_1$.

[6] Romannikov, V. N.; Mastikhin, V. M.; Hočevar, S.; Držaj, B. *Zeolites* **1983**, *3*, 311−320.

[7] For NMR experiments, the glass tube with a zeolite sample was opened, and the sample was transferred into a 7 mm zirconia rotor. The ^{13}C NMR spectrum with cross-polarization and magic angle spinning (^{13}C CP/MAS NMR) was then recorded on a Bruker MSL-400 NMR spectrometer at room temperature (~296 K). The following conditions were used for CP experiments: the proton high-power decoupling field was 12 G (4.9 μs 90° ^{1}H pulse); contact time 5 ms at Hartmann−Hahn matching conditions 51 kHz, delay between scans 3 s, spinning rate 2.4−2.6 kHz. One-pulse-excitation spectra with high-power proton decoupling were recorded using a 45° pulse of 2.5 μs length and repetition time 10 s.

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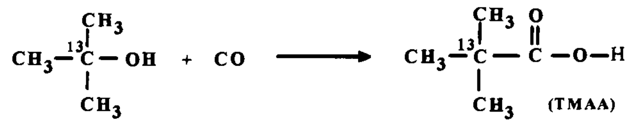
Scheme 1



the signal 40.7 ppm is well understood, provided that adsorbed *t*-BuOH-2-^{13}C reacts with CO as shown in Scheme 1.

According to Scheme 1, mainly the signal from the ^{13}C -labeled quaternary carbon atom of TMAA should be observed. Indeed, there is good agreement between the chemical shift for the signal at 40.7 ppm in Figure 1A and that for the signal of the quaternary carbon atom in liquid TMAA (38.5 ppm[8]). This fact supports the formation of TMAA. The signal at 81.4 ppm, which is typical for a *tert*-butyl group bound to oxygen, should be attributed to either *tert*-butyl silyl ether, i.e., the *tert*-butyl group bound to the oxygen of the zeolite framework[9] or unreacted alcohol.[10]

One of the two signals observed for coadsorption of *t*-BuOH, labeled with ^{13}C in a methyl group (*t*-BuOH-*1*-^{13}C), and the unlabeled CO, namely the signal at 27.8 ppm (Figure 1B), further supports the formation of TMAA. Indeed, methyl groups of liquid TMAA exhibit the signal at 27.8 ppm,[8] i.e., their position coincides with the position of one of the two signals in Figure 1B. The second signal, with a chemical shift of 29.7 ppm, belongs (similar to the case with *t*-BuOH-2-^{13}C) to CH_3 groups of either *tert*-butyl silyl ether[9] or unreacted alcohol.[10]

When the labeled ^{13}CO and unlabeled *t*-BuOH were used, we observed basically two signals at 194 and 186 ppm, the latter being seen as a shoulder of the first one (Figure 1C). These two signals are in the region typical for carbonyl groups;[11] however, their line shapes with numerous spinning side bands differ from those of unreacted ^{13}CO.[12] These data are also in favor of the reaction between *t*-BuOH and CO. Thus, two signals appear in the region, where a signal from TMAA −COOH group should be expected (185.7 ppm in liquid TMAA[8]). Both of these signals certainly belong to TMAA, because TMAA specially adsorbed on H-ZSM-5 in a separate experiment (spectrum is not shown) exhibits the same two signals at 194 and 186 ppm, in addition to the signals at 40.7 and 27.8 ppm from the quaternary carbon atom and CH_3 groups, respectively. From our NMR data, the attribution of these two signals from the −COOH of TMAA to some certain adsorbed species cannot be made unambiguously. Nevertheless, a tentative assignment of these signals can be made. Usually, more acidic bridged Si−OH−Al groups produce larger perturbation on ^{13}C chemical shifts of adsorbed molecules[13,14] compared to the less acidic Si−OH groups.[14] Therefore, the signal at 194 ppm may belong to the acid adsorbed on bridged Si−OH−Al groups, and the signal at 186 ppm may be assigned to the acid on terminal Si−OH groups. At the same time, one cannot reject that these two signals belong to monomeric and dimeric states of the acid[15] inside H-ZSM-5 or to the acid on the adsorption sites located at different spatial surroundings inside the zeolite framework (e.g., in the zeolite channels or at channel intersections[16]). To make an attribution of the signals at 194 and 186 ppm more reliably, a further special study is needed, which is beyond the scope of this paper.

For coadsorption of isobutylene, ^{13}CO, and H_2O on H-ZSM-5, similar signals in ^{13}C CP/MAS NMR spectra are observed, and therefore the same product must be formed (Figure 1E). Note that in Figure 1E the signal at 29.7 ppm is also observed, similar to the case with *t*-BuOH. This signal may be assigned to methyl groups of *t*-BuOH, which can be formed as a result of olefin hydration on the zeolite.[17]

To confirm the formation of TMAA inside H-ZSM-5, the zeolite was dissolved in 10% NaOH solution. The formed solution was neutralized with H_2SO_4, and organic products were extracted with Et_2O. Subsequent evaporation of Et_2O and GC-MS analysis of the residue showed that TMAA was the main reaction product.

Thus, our experiments clearly indicate that the Koch reaction can easily be carried out with *t*-BuOH or *i*-C_4H_8 at room temperature on H-ZSM-5 with high yield (50% for *t*-BuOH and 85% for *i*-C_4H_8[5]). This observation may open up new possibilities for use of solid acids as carbonylation catalysts under mild conditions.

Note in conclusion that when t-BuOH and CO are coadsorbed on H-ZSM-5, the selective ^{13}C labels do not undergo scrambling over the carbon skeleton of the reaction participants, as the label does when *t*-BuOH is adsorbed on H-ZSM-5 without CO.[9,10] Moreover, no signals appear at 10−40 ppm from isobutylene oligomers, which are formed from *t*-BuOH on H-ZSM-5 in the absence of CO.[9,10,18] Both of these facts show that interaction of CO with *t*-BuOH represents a faster process than ^{13}C scrambling and isobutylene oligomerization.

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