Interaction of Olefins with Carbon Monoxide on Zeolite H-ZSM-5. NMR Observation of the Friedel−Crafts Acylation of Alkenes at Ambient Temperature

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Received May 8, 1996

Recently, it has been shown that interaction of small olefins and carbon monoxide on zeolite H-ZSM-5 in the presence of water (the Koch reaction[1,2]) results in high conversion of an olefin into a carboxylic acid at 296 K.[3] The procession of the Koch reaction on a zeolite under mild conditions[3] can be reasonably explained (by analogy with acidic solutions[2,4]) through the trapping of an alkyl carbenium ion, generated from an olefin (or alcohol) inside a zeolite, by CO to form an acylium cation.[2,4] The latter is quenched with water to give a carboxylic acid[2,4] (see Scheme1, pathway 1). However, in the absence of water, one could expect that the generated (*in situ*) acylium cation would interact with another olefin molecule to give an unsaturated ketone.[5]

In this paper, we report that, under waterless conditions, olefins (ethene, isobutene, 1-octene) indeed interact with CO on H-ZSM-5 at 296 K to give unsaturated ketones and stable cyclic five-membered ring carboxonium ions (pathway 2 in Scheme 1). Thus, we have obtained the first evidence for the Friedel−Crafts acylation of alkenes[5,6] in zeolite catalyst at ambient temperature by acylium cation, generated *in situ* from olefins and CO.

A well-characterized H-ZSM-5 zeolite (Si/Al = 49)[7] was activated by heating at 450 °C under vacuum (10^{-5} Torr) for 4 h. Then, we froze out equal amounts of olefin and CO on H-ZSM-5 under vacuum at liquid nitrogen temperature. After the glass tube containing the zeolite sample under vacuum was sealed, the sample was slowly warmed to room temperature and kept at 296 K for a few hours allowing the reaction to proceed. The reaction products were analyzed directly inside the zeolite sample with ^{13}C CP/MAS NMR[8] in a sealed glass tube inserted into the NMR zirconia rotor. In addition, we dissolved the zeolite framework and then analyzed the liberated organic products with GC-MS and ^{13}C NMR.

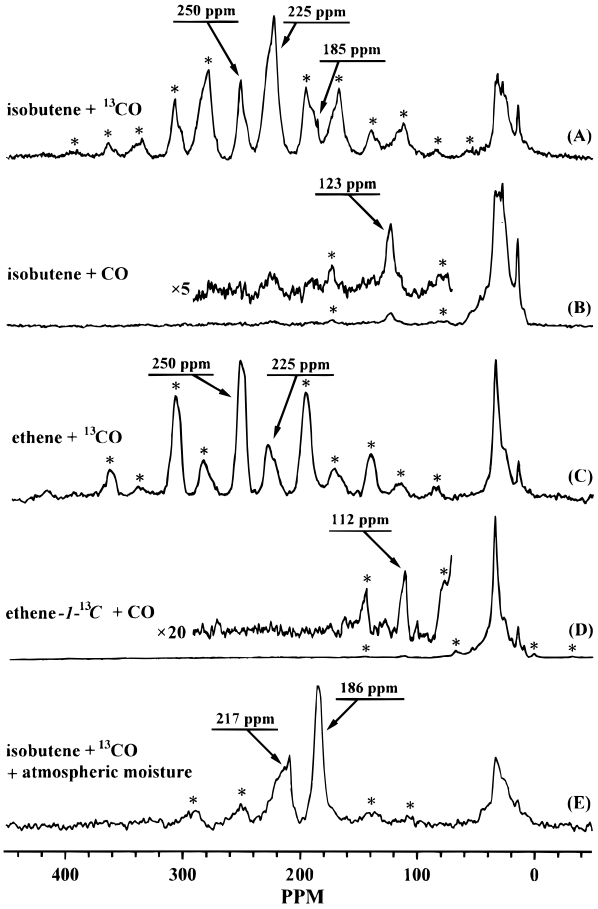

Figure 1. ^{13}C CP/MAS NMR spectra for the products formed at 296 K after coadsorption of an olefin and CO on H-ZSM-5 zeolite: (A) coadsorption of the unlabeled isobutene and ^{13}CO (90% ^{13}C enrichment); (B) coadsorption of the unlabeled isobutene and unlabeled CO; (C) coadsorption of the unlabeled ethene and ^{13}CO; (D) coadsorption of the ethene-*1*-^{13}*C* (90% ^{13}C enrichment) and unlabeled CO; (E) after the sample (A) was kept for 1 month under air atmosphere at ambient temperature. Approximately 300 μmol/g (*ca.* 1 equiv per Al atom) of an olefin and CO were adsorbed in each case; 15000−24000 scans have been collected for each spectrum. Asterisks (*) denote spinning sidebands.

Scheme 1

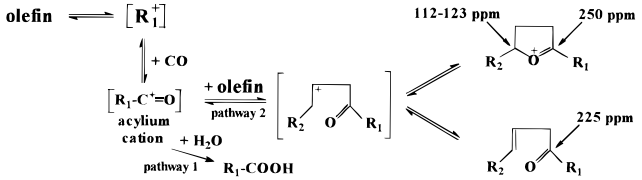

Figure 1 reports ^{13}C CP/MAS NMR spectra recorded after coadsorption of olefins and carbon monoxide on H-ZSM-5. If ^{13}C-labeled CO and unlabeled isobutene are used for coadsorption (Figure 1A), then two intense signals at 225 and 250 ppm from the ^{13}C-labeled carbonyl group are observed; their line shapes with numerous spinning sidebands differ from those of unreacted ^{13}CO. The small-intensity narrow line from ^{13}CO is seen in this spectrum at 185 ppm.[9] The signals at 225 and 250 ppm indicate that the reaction between isobutene and CO

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(8) ^{13}C NMR spectra with cross polarization and magic angle spinning (^{13}C CP/MAS NMR) were recorded on a Bruker MSL-400 NMR spectrometer at 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 3−5 ms at Hartmann−Hahn matching conditions 51 kHz, delay between scans 3 s, spinning rate 5.0−5.6 kHz.

(9) The narrow line at 185 ppm without spinning sidebands from unreacted ^{13}CO can especially be well seen in the spectra recorded without cross-polarization for all coadsorbed olefins and CO (these spectra are not shown). The chemical shift of ^{13}CO is in good accordance with that observed earlier inside H-ZSM-5. (a) Anderson, M.W.; Klinowski, J. *J. Am. Chem. Soc.* **1990**, *112*, 10−16. (b) Munson, E. J.; Lazo, N. D.; Moellenhoff, M. E.; Haw, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 2783−2784.

S0002-7863(96)01538-7 CCC: $12.00

proceeds on the zeolite at 296 K and ^{13}CO transforms into ^{13}C-labeled carbonyl group of some organic product. The signals from aliphatic moieties (natural ^{13}C abundance) in the reaction products are seen at 12−40 ppm.

In principle, interaction of acylium cation with olefins in the presence of acid catalysts (known as Friedel−Crafts acylation of alkenes[5]) can proceed via two different routes (see Scheme 1). One of them leads to the formation of unsaturated ketones.[5] The situation is proven to be the same for the zeolite catalyst. One of the signals shown in Figure 1A, at 225 ppm, can be attributed to the carbonyl group of unsaturated ketones that is either strongly interacting with the Brönsted acid site of the zeolite or partially protonated.[10,11] Indeed, liquid unsaturated ketones exhibit ^{13}C chemical shifts between 195 and 215 ppm.[12] If the interaction of the carbonyl group of ketones adsorbed in zeolite additionally moving the signal downfield a maximum of 19 ppm is taken into account,[10] then the position of the signal at 225 ppm for unsaturated ketones seems reasonable. At the same time, even under a complete protonation of unsaturated ketones in the superacids, the shift for carbonyl group never exceeds 231 ppm.[13] The appearance of the signal at 250 ppm for the carbonyl groups is easily rationalized in terms of the second competing pathway of acylation reaction resulting in the formation of carboxonium ion,[6,14] the signal from the carbonyl group with the positive charge on oxygen atom (-O^+=C-) in such cations being observed near 245−250 ppm.[6,14]

For CO and isobutene, both with natural ^{13}C abundance, the signal at 123 ppm provides further evidence for the formation of cyclic five-membered ring[6] carboxonium ion. An alternative to this cyclic carboxonium ion is noncyclic[14] or six- or seven-membered cyclic[14] carboxonium ions, but they are not identified for coadsorbates used in this study.[15]

For the coadsorption of CO and ethene (Figure 1C, D) or 1-octene (spectrum is not shown), the same signals are observed: 250 and 112 ppm for cyclic carboxonium ions[15] and 225 ppm for unsaturated ketones.

Thus, we have obtained evidence for cyclic carboxonium ion (in addition to already known alkyl-substituted cyclopentenyl cation[16,17] and trimethyloxonium ion[18]) to be generated inside acidic zeolite. It should be noted that none of the signals observed in Figure 1 can be attributed either alkyl[19] or acylium cations[20] that are included in Scheme 1 as intermediates. They represent highly reactive transient species inside the zeolite.[21]

The observed carbonylation/acylation processes are inevitably complicated by oligomerization reaction, which usually gives rise to long-chain oligomers in the absence of CO.[22] Hence, the reaction of carbon monoxide with olefin oligomers (linear for ethene and 1-octene) should result in the acylation products with long hydrocarbon fragments R_1 and R_2 (R_1, $R_2 = C_n H_{2n+1}$, where $n \geq 4$).

Note that there no signals appear from the C=C double bond of unsaturated ketones[23] (see Figure 1B, D). We believe that the situation may be similar to that existing for oligomers formed at ambient temperature from small olefins on acidic zeolite. These oligomers exhibit no characteristic signals from the double bond moiety in their ^{13}C NMR spectra.[22,24]

If the zeolite sample is exposed to atmospheric moisture, both signals at 225 and 250 ppm slowly decrease, and finally, two groups of the signals at 186 and 217 ppm are identified in the spectrum (Figure 1E). The former signal shows that the carboxylic acids are formed,[3] and the latter one may be interpreted as an upfield shift of the signal at 225 ppm from unsaturated ketones resulting from the penetration of water in zeolite pores, which destroys the strong interaction of ketone carbonyl group with Brönsted acid sites. Note that the interaction of carboxonium ion with water inside zeolite does not result to the formation of oxyketones, as was observed earlier for the transformation of these cyclic ions in solutions.[6] The signals from COH fragments of oxyketones would be located near 70 ppm.[25] Addition of water into the zeolite seems to shift the equilibria in Scheme 1 toward the acylium cation, from which carboxylic acids are formed.

To confirm the formation of the acylation products on zeolite, the sample with coadsorbed isobutene and CO was dissolved in 10% NaOH solution. After the formed solution was neutralized with H_2SO_4 and the organic products were subsequently extracted with Et_2O, and the excess ether was evaporated, GC-MS and ^{13}C high-resolution NMR analyses of the residue were carried out. These analyses revealed that C_9 unsaturated ketones, C_9 oxyketones (the products of hydrolysis of both unsaturated ketones and cyclic carboxonium ions), and the equilibrium products of their reverse aldol condensation reaction (acetone and C_6 aliphatic ketones) prevailed in the mixture educed from H-ZSM-5. Carboxylic acids and olefin oligomers were also among the main reaction products.

Thus, our NMR experiments clearly indicate that the Friedel−Crafts acylation of alkenes can be performed by acylium cation, generated *in situ* from olefin and CO in H-ZSM-5 pores at ambient temperature. Inside a zeolite, the main reaction products represent cyclic carboxonium ions and unsaturated ketones. Our results indicate the potential for the use of acidic zeolites as catalysts for the synthesis of carbonyl containing organics (unsaturated ketones) from olefins and carbon monoxide.

Acknowledgment. The authors sincerely thank Dr. V. N. Sidelnikov for GC-MS analysis. This research was supported by grant 95-03-08780 from the Russian Foundation for Basic Research (RFBR) and by joint RFBR-INTAS grant (95-IN-RU-194).

JA9615381

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(15) ^{13}C chemical shifts for carbon atom in the -C−O^+= group of cyclic five-membered ring carboxonium ions (111−121 ppm, see ref 6) are clearly distinguished from noncyclic or six- or seven-membered cyclic carboxonium ions (82−95 ppm, see ref 14). Thus, on the basis of the shift for the -C−O^+= group we are able to identify the structure of the observed carboxonium ions.

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