DOI: 10.1002/anie.200700029

Carbonylation of Methanol on Metal–Acid Zeolites: Evidence for a Mechanism Involving a Multisite Active Center**

Teresa Blasco, Mercedes Boronat, Patricia Concepción, Avelino Corma, David Law, and Jose Alejandro Vidal-Moya*

Carbonylation of alcohols and olefins in the presence of water with CO to produce acids and acetates is carried out at high pressure in the presence of strong Brønsted and Lewis acid catalysts.[1] Organometallic complexes containing Rh or Ir together with iodide compounds are able to catalyze such reactions at low temperatures and atmospheric pressure,[2,3] and they are now used for the synthesis of acetic acid from methanol and CO. However, the finding that zeolites are able also to catalyze the carbonylation of alcohols at low temperatures and atmospheric pressure has renewed interest in the use of solid catalysts, and more specifically zeolites, for developing a halide-free carbonylation catalyst.[4–7]

Concerning the reaction mechanism with zeolites, it has been found that the alcohol adsorbs on Brønsted acid sites to form a methoxy species, which reacts with CO to form an acylium cation that can be quenched by H_2O to give the corresponding acid.[4,6,8–10] The limiting step of the reaction is believed to be the attack of the methoxy species by CO to form an acylium cation type species. Very interesting results were recently presented for the reaction of dimethyl ether (DME) with CO on H-Mordenite in the absence of H_2O; the reaction revealed excellent selectivity to give methyl acetate at low temperatures (423–463 K).[11] A reaction mechanism in which the limiting step of the reaction involved attack of CO at a methoxy group was proposed on the basis of kinetic experiments[11] and was confirmed later by NMR spectroscopy results.[12] As a result of the high selectivity for methyl acetate when using DME under H_2O-free reaction conditions,[12] this work represents an important step forward. Nevertheless, it would be preferable, from a process point of view, to use methanol instead of DME as feed. However, when methanol was used, conversion was much lower and higher reaction temperatures were required with the corresponding formation of hydrocarbons.[7] As the controlling step of the reaction is the attack of CO at the adsorbed methoxy species, there is a possibility to increase the rate of reaction through a bifunctional catalyst in which the methoxy groups would be formed on a Brønsted acid site of the zeolite while CO would be activated at a metal site located in a next near neighbor aluminum framework.

We report here a detailed mechanistic study of methanol carbonylation on H-Mordenite and Cu-H-Mordenite that was carried out by using IR operando spectroscopy and "in situ" magic-angle spinning (MAS) NMR spectroscopy. We observed the formation of intermediate methoxy and acylium species and found that Cu not only activates CO under reaction conditions but also absorbs DME preferentially to H_2O and methanol. This preferential adsorption favors the attack of DME at the acylium cation in the case of Cu-H-Mordenite to give methyl acetate as the primary product. Meanwhile, in the case of H-Mordenite, water adsorption prevails and acetic acid is produced as the primary and predominant product. It is remarkable that under the reactions conditions studied here (200 °C–240 °C), the formation of hydrocarbons was not observed while almost total conversion of methanol and DME occurred.

The IR spectrum of Cu-H-Mordenite activated with CO at 350 °C (see Experimental Section) shows an intense and narrow band at 2159 cm^{-1} assigned to a Cu^+-monocarbonyl species.[13,14] This band shifts to 2129 cm^{-1} after the co-adsorption of methanol/CO at 100 °C, and the shift is completely reversed upon methanol desorption, suggesting that methanol, an electron-donor group, adsorbs onto the Cu^+-CO complexes (see Figure 1 in the Supporting Information).

The IR spectra recorded after heating the methanol/CO mixture at 200 °C over H-mordenite and Cu-H-Mordenite show the presence of dimethyl ether as well as the formation of methoxy groups over Brønsted acid sites (2975 cm^{-1}) and AlOH (2969 cm^{-1}) and silanol (2956 cm^{-1}) groups.[15,16] The ν(C–H) stretching vibration band of dimethyl ether appears at 2834 cm^{-1} in H-Mordenite and at 2840 cm^{-1} in Cu-H-Mordenite, suggesting that this molecule interacts with Cu^+ ions, as supported by the appearance of a second band at 2133 cm^{-1} in the carbonyl stretching vibration region (see Figure 2 in the Supporting Information). Therefore, besides monocarbonyl Cu^+ species (2159 cm^{-1}), dimethyl ether (electron donor) adsorbed on Cu^+-CO species is formed. For both Cu-H-Mordenite and H-Mordenite, a band corresponding to adsorbed water appears at 1630 cm^{-1} upon cooling down the

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[*] Dr. T. Blasco, Dr. M. Boronat, Dr. P. Concepción, Prof. A. Corma, Dr. J. A. Vidal-Moya
Instituto de Tecnología Química, UPV-CSIC
Universidad Politécnica de Valencia
Avda. de los Naranjos s/n, 46022 Valencia (Spain)
Fax: (+34) 96-387-7809
E-mail: acorma@itq.upv.es

Dr. D. Law
BP Chemicals
Hull Research & Technology Centre
Saltend, Hull HU12 8DS (UK)

[**] The authors thank BP Chemicals for financial support and for permission to publish these results. J.A.V.-M. thanks the CSIC (grant I3P). Thanks also to the CICYT (project MAT2006-14274-C02-01) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

sample to room temperature, which suggests that H_2O remains in the gas phase at 200 °C.

To detect possible reaction intermediates over H-Mordenite and Cu-H-Mordenite, time-resolved IR spectra were recorded at 240 °C (see Figure 1). For H-Mordenite, the band at 1458 cm^{-1} from the CH deformation vibration of dimethyl ether decreases in intensity, while new bands at 1490, 1427, 1387, and 1366 cm^{-1} increase with time. These bands together with that at 3266 cm^{-1}, which is characteristic of acidic compounds, (see inset of Figure 1 a) indicate the formation of acetic acid. In Cu-H-Mordenite, the intensities of the bands for the Cu^+-carbonyl complexes, both isolated (2159 cm^{-1}) and co-adsorbed with DME (2133 cm^{-1}), decrease with reaction time, while the intensities of two bands at 1496 and 1387 cm^{-1} associated with COO^- groups (acetate) and a weak band at 3266 cm^{-1} for acetic acid increase with reaction time (see Figure 1 b). We note the presence of a band (C=O) at 1685 cm^{-1} which disappears after 90 minutes reaction (Figure 1 b). This intermediate must be formed by reaction of carbon monoxide (C≡O) with a carbocation, which probably forms from the dissociation of DME or from methoxy groups of the zeolite surface.

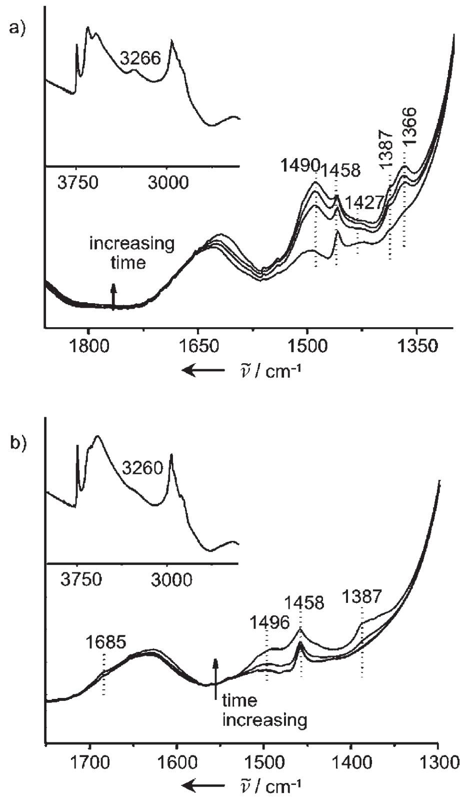


Figure 1. Time-resolved FTIR spectra of a) H-Mordenite at 6, 17, 23, and 49 min and b) Cu-H-Mordenite at 1, 5, 15, and 40 min, after CO/MeOH co-adsorption at 240 °C. The insets show the 4000–2500 cm^{-1} IR region.

Up to now and from the IR operando spectroscopy study, we can conclude that the carbonylation reaction proceeds differently on H-Mordenite and Cu-H-Mordenite zeolites. CO forms monocarbonyl Cu^+-CO complexes up to 350 °C on the Cu-H-Mordenite zeolite. At 200 °C, DME, methoxy species, and water are formed on both zeolites, but DME is co-adsorbed on the Cu^+-CO sites in Cu-H-Mordenite, preferentially to H_2O. The CO group involved in the monocarbonyl Cu^+-CO complex can react with close methoxy groups to form a CH_3CO^+ reactive intermediate, which we were not able to detect in the H-Mordenite zeolite probably because of the lower concentration. DME that is stabilized on Cu-H-Mordenite reacts with the acylium cation formed on the acid sites of the zeolite leading to the preferential formation of acetate. Meanwhile, formation of the acid is preferred on the H-Mordenite zeolite.

The results and conclusions obtained by IR spectroscopy are fully supported by the in situ NMR experiments, carried out using labeled molecules. To identify the species strongly bonded to the zeolites, we recorded ^{13}C NMR spectra after the reaction of $^{13}CO/^{13}CH_3OH$ at 180 °C over H-Mordenite and Cu-H-Mordenite using a low reactant concentration ($^{13}CH_3OH/Al = 0.25$, $^{13}CO/^{13}CH_3OH = 3$; see Figure 3 in the Supporting Information). For both zeolites, the simulated spectra provide evidence for the presence of dimethyl ether with side-on and end-on configurations, methoxy species formed on Brønsted hydroxy and silanol groups, and methanol adsorbed end-on and side-on.

The ^{13}C MAS NMR spectra of the $CO/^{13}CH_3OH$/H-Mordenite (molar ratios: $^{13}CO/^{13}CH_3OH = 3$, $^{13}CH_3OH/Al = 0.5$) system heated at 200 °C up to 15 min consist of a very intense signal for dimethyl ether at $\delta = 59.6$ ppm and a weaker signal for methanol at $\delta = 50.7$ ppm. After heating for 15 min, a new signal emerges at approximately $\delta = 20$ ppm, which is assigned to the methyl group involved in $^{13}\mathbf{C}H_3\text{-}^{13}COO^-$ acetyl groups. This signal gradually increases with reaction time, while those for methanol and dimethyl ether decrease (see Figure 4 in the Supporting Information). Inspection of the NMR region corresponding to the methyl-acetyls ($^{13}\mathbf{C}H_3\text{-}COO^-$) reveals the presence of two components at $\delta = 20.6$ and 19.2 ppm, which can be assigned to acetic acid ($^{13}\mathbf{C}H_3\text{-}^{13}COOH$) and methyl acetate ($^{13}\mathbf{C}H_3\text{-}^{13}COO^{13}CH_3$), respectively. The formation of the latter product is confirmed by the appearance of a peak at $\delta = 53.4$ ppm, from the methoxy group of methyl acetate ($^{13}CH_3\text{-}^{13}COO^{\mathbf{13}}\mathbf{C}H_3$), which becomes more pronounced at long reaction times (see Figure 4 in the Supporting Information).

Although the same species are formed on Cu-H-Mordenite, the ^{13}C NMR signal for the methyl group from $^{\mathbf{13}}\mathbf{C}H_3\text{-}^{13}COO^-$ appears after 5 min at 200 °C. Moreover, the spectra simulation using two individual lines for $^{\mathbf{13}}\mathbf{C}H_3\text{-}^{13}COOH$ ($\delta = 20.6$ ppm) and $^{\mathbf{13}}\mathbf{C}H_3\text{-}^{13}COO^{13}CH_3$ ($\delta = 19.2$ ppm) indicates that the acid predominates on H-Mordenite while the acetate predominates on Cu-H-Mordenite, in agreement with the IR results (see Figure 5 in the Supporting Information).

Concerning the carbonyl region of the ^{13}C MAS NMR spectra, besides the presence of ^{13}CO within the zeolite channels, the Cu-H-Mordenite sample shows an additional broad band at $\delta = 171$ ppm which can be assigned to ^{13}CO molecules adsorbed over Cu^+ cations[17] (see Figure 6 in the Supporting Information). By taking into account previous results and the fact that CO and DME are preferentially adsorbed on Cu^+, we should expect a higher rate of reaction for the formation of acetyls with Cu-H-Mordenite than with H-Mordenite during carbonylation of methanol. Thus, the kinetics of the process was followed by "in situ" MAS NMR, and the results clearly show more than a threefold increase in the reaction rate when Cu is introduced (Figure 2).

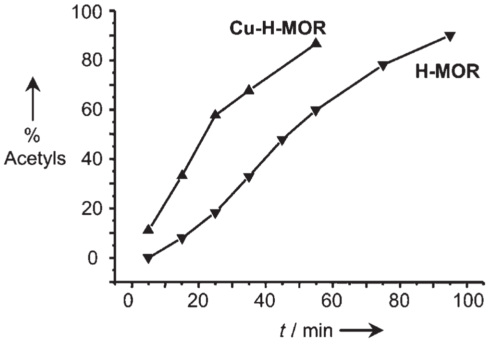
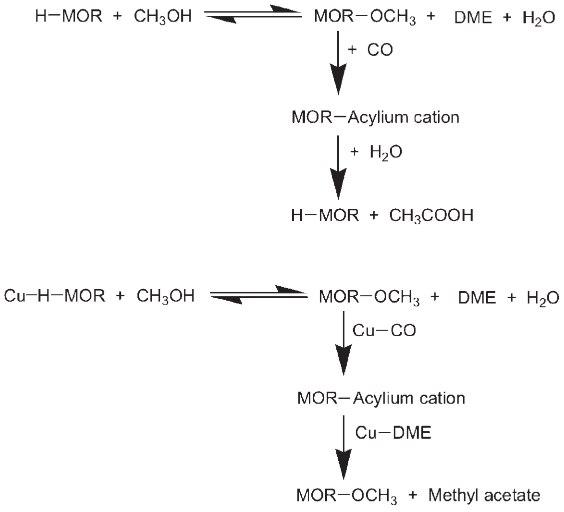


Figure 2. Conversion of $^{13}CH_3OH$ to acetyls in the $^{13}CO/^{13}CH_3OH$ reaction at 200 °C over H-Mordenite (H-MOR) and Cu-Mordenite (Cu-H-MOR), as measured by in situ ^{13}C MAS NMR spectroscopy.

In conclusion, we have confirmed the reaction mechanisms proposed for the carbonylation of methanol on protonic zeolites[8–10] by detecting the intermediate species formed on the catalyst surface by means of IR operando spectroscopy and "in situ" MAS NMR spectroscopy. We have also shown that a different reaction mechanism occurs on a metal zeolite (Cu-H-Mordenite). Thus, while acetic acid is formed as a primary acetyl product when reacting methanol on H-Mordenite, methyl acetate is formed in the case of Cu-H-Mordenite. It is shown that in the case of Cu-H-Mordenite, the reaction rate is much higher than with H-Mordenite. The above results can be explained on the basis of a reaction mechanism in Cu-H-Mordenite that involves an active site composed of two neighboring sites, one bridged hydroxy and a neighboring Cu^+. The Brønsted acid site is responsible for activating the methanol (methoxy), while Cu^+ can activate the CO and adsorbs preferentially the DME compared to methanol and water under our reaction conditions. A mechanism is proposed in Scheme 1 for the carbonylation of methanol on a purely acid zeolite (H-Mordenite) and on a metal-containing acid zeolite (Cu-H-Mordenite).

Experimental Section

H-Mordenite was obtained by calcination of a commercial sample of mordenite (ammonium form; $Si/Al_2 = 20$; CBV20A from Zeolyst International) at 500 °C during 2 h. Cu-H-Mordenite catalyst was prepared by a two-step ion-exchange method as follows: first, commercial mordenite (9.58 g) was mixed with an aqueous solution (100 mL) of copper nitrate (1.507 g of $Cu(NO_3)_2{\cdot}3H_2O$), and the mixture was heated at reflux at 80 °C during 2 h. The slurry obtained was filtered and dried at 100 °C for 12 h. Then, the resulting solid was mixed again with an aqueous solution of copper nitrate solution (0.78 g of $Cu(NO_3)_2{\cdot}3H_2O$; 87 mL). The mixture was heated again at reflux at 80 °C for 2 h and filtered, and the slurry was dried at 100 °C for 12 h. Finally, the material obtained was calcined at 500 °C for 2 h. The amount of Cu in the sample was 2.5 % by weight.



Scheme 1. A potential reaction mechanism for carbonylation of methanol with CO on H-Mordenite (H-MOR) and Cu-H-Mordenite (Cu-H-MOR).

FTIR experiments were performed with a Biorad FTS-40 A spectrometer using an IR flow quartz cell connected to a vacuum line with gas-dosing possibilities. Prior to adsorption experiments, H-Mordenite and Cu-H-Mordenite zeolites were activated at 350 °C in N_2 flow (20 mL min^{-1}) for 2 h, followed by two additional hours of treatment with 4 % CO/He flow (20 mL min^{-1}) at the same temperature. Afterwards, the samples were evacuated at 100 °C at 10^{-4} mbar for 30 minutes. CO and methanol in a molar ratio of 10:1 were adsorbed at 100 °C. For mechanistic studies, time-resolved IR spectra were recorded at increasing temperatures.

For ^{13}C MAS NMR experiments, samples H-Mordenite and Cu-H-Mordenite were dehydrated at 400 °C overnight, treated with ^{13}CO (500 mbar) at 350 °C during 2 h, and subsequently degassed at 350 °C for 1 h. Then, ^{13}CO (2200 μmol per gram zeolite) and subsequently $^{13}CH_3OH$ (730 μmol per gram zeolite), corresponding to $^{13}CH_3OH/Al = 0.5$, were introduced onto the activated zeolite, resulting in a molar ratio $^{13}CO/^{13}CH_3OH = 3$. The glass inserts were sealed while they were immersed into liquid nitrogen. To monitor the reaction, NMR spectra were recorded following treatment of the sample at 200 °C during increasing reaction times outside the NMR probe. Solid-state NMR spectra were recorded at room temperature with a Bruker AV 400 WB spectrometer. The glass inserts were fitted into 7 mm rotors and were spun at 5 kHz in a Bruker BL7 probe. ^{13}C MAS NMR spectra were recorded with proton decoupling, with 90° pulse length of 5 μs and a recycle delay of 30 s.

Received: January 3, 2007
Revised: February 28, 2007

Keywords: carbonylation · copper · heterogeneous catalysis · reaction mechanisms · zeolites

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