



A green route for methanol carbonylation†

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Acetic acid is one of the most important bulk commodity chemicals and is currently manufactured by methanol carbonylation reactions with rhodium or iridium organometallic complexes and halide-containing promoters named Monsanto or BP Cativa™ homogeneous processes, respectively. Developing a halide-free catalyst and a heterogeneous process for methanol carbonylation is of great importance and has recently attracted extensive research attention. Here, we report a green route for direct synthesis of acetic acid *via* vapor-phase carbonylation of methanol with a stable, selective, halide-free, and noble metal-free catalyst based on pyridine-modified H-mordenite zeolite. Methanol conversion and acetic acid selectivity can reach up to 100% and 95%, respectively. Only little deactivation is observed during the 145 hour reaction.

1 Introduction

Acetic acid (HAc), which is widely used in the manufacture of vinyl acetate monomer, acetic anhydride, and acetic esters, is one of the most important bulk commodity chemicals with a worldwide production of more than 10 million tonnes per year.¹ Currently, HAc is manufactured by methanol carbonylation with rhodium or iridium organometallic complexes and halide-containing promoters named Monsanto² or BP Cativa™³ homogeneous processes, respectively. However, these two commercial processes need to be further improved:¹ a homogeneous system requires excessive energy to separate the products and catalysts; a halide-containing system causes serious equipment corrosion because of the formation of HI in this catalytic cycle; the commonly used noble metal catalysts are scarce and extremely expensive; the presence of water results in complicated purification and lower utilization of CO due to the water gas shift reaction.

Many studies have been focused on these challenges in the past few decades. Heterogeneous catalysts, which were prepared by immobilizing active sites on solid materials, such as polymers, silicon oxides or carbons, were designed for facilitation of separation.^{4–7} Halide-containing rhodium or iridium catalytic systems cannot be substituted by base

metals⁸ because of their high activity and catalytic efficiency under mild reaction conditions. Therefore, developing highly effective and stable heterogeneous catalysts in the absence of noble metals and halide promoters for this process is of great importance. As is known, carbonylation of methanol can also be realized *via* Koch-type pathways using acidic catalysts. Fujimoto *et al.* first reported that methanol carbonylation to HAc could proceed over zeolites, such as H-mordenite (H-MOR).⁹ The enhanced activity can be achieved by using Cu-modified H-MOR (Cu-MOR).^{10–13} However, two contradictions still exist: at low reaction temperature, H₂O derived from methanol dehydration which has a negative influence on the reaction significantly decreases the carbonylation rate; at high reaction temperature, the formation of polymethylbenzenes apparently blocks the pores, resulting in significant catalytic deactivation.¹⁴ An indirect way *via* carbonylation of dimethyl ether (DME) to methyl acetate (MAc) under anhydrous conditions has been extensively studied because of the high efficiency of carbonylation at low temperature.^{15–26} Nevertheless, two extra reactions, methanol dehydration to DME and MAc hydrolyzation to HAc, should be considered.

Mordenites, which contain 8- and 12-membered ring (MR) channels, are proved to be the best zeolite catalysts for methanol carbonylation.^{9–13} According to quantum-chemical methods, hydrocarbons are more easily formed in the 12-MR than 8-MR channels.²⁷ Liu *et al.* also reported that the stability of H-MOR catalysts for DME carbonylation could be improved by pyridine selectively blocking the 12-MR channels.²¹ Different from DME carbonylation under anhydrous conditions, up to now, it is still a challenge to develop a highly stable and selective zeolite catalyst for direct carbonylation of methanol to HAc.

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Here, we report a stable, selective, halide-free, and noble metal-free catalyst based on pyridine-modified H-MOR (Py-MOR) for synthesis of HAc *via* direct carbonylation of methanol. Methanol conversion and HAc selectivity can reach up to 100% and 95%, respectively.

2 Experimental

2.1 Catalyst preparation

Na-Mordenite (Na-MOR) was converted into its NH_4^+ form by exchanging 100 g Na-MOR with 1 L NH_4NO_3 (1 mol L^{-1}) aqueous solution at 353 K for 2 h, followed by filtration and washing with deionized water. After repeating the above-mentioned process three times, the desired sample was dried at 383 K for 10 h, followed by calcination at 823 K for another 4 h in air to obtain the H-mordenite (H-MOR) catalyst with a Si/Al ratio of 6.9 (detected by X-ray fluorescence). Next, H-MOR was treated in an 8 mm inner diameter stainless steel fixed-bed reactor as follows: 2.0 g H-MOR was heated to 573 K at a rate of 10 K min^{-1} under N_2 (90 mL min^{-1}) flow and kept for 2 h. After cooling to 553 K, a flow of N_2 (30 mL min^{-1}) saturated with pyridine vapor (about 1.5% by volume) was introduced into the reactor for 3 h, followed by purging with N_2 (60 mL min^{-1}) for another 4 h at the setting temperature. Here, this pyridine-modified H-MOR catalyst was named Py-MOR. The Cu-MOR catalyst was prepared by ion-exchange. 10.0 g of H-MOR was suspended in 1 L of 0.04 mol L^{-1} $\text{Cu}(\text{NO}_3)_2$ aqueous solution at 353 K for 5 h. After filtration and washing with deionized water, the resulting solid was calcined at 773 K in air for 4 h to obtain the Cu-MOR catalyst with 1.3% Cu content (detected by X-ray fluorescence).

2.2 Catalyst characterization

A PANalytical X'Pert PRO X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation was applied to record the X-ray diffraction patterns. A PANalytical Axios Advanced X-ray fluorescence (XRF) spectrometer was used to determine the chemical composition. SEM images were taken with an SU8020 scanning electron microscope. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker VERTEX 70 instrument with a MCT detector and a resolution of 4 cm^{-1} . After the catalysts were pretreated with 30 mL min^{-1} N_2 at 493 K for an hour, the FT-IR spectra were recorded at 493 K. An SDT-Q600 instrument with a THERMO StarTM gas analysis system was used to conduct thermal gravimetric (TG) analysis. About 30 mg sample was pretreated with 100 mL min^{-1} N_2 at 473 K for 1 h, and then heated to 1273 K in 100 mL min^{-1} air at a ramping rate of 10 K min^{-1} . 0.05 g spent zeolite catalysts were dissolved in 0.05 mL HF solution (20%). After being neutralized with 5 wt% NaOH solution, the soluble cokes were extracted with 0.5 mL CH_2Cl_2 containing 10 ppm C_2Cl_6 (internal standard) and then analyzed using a GC-MS (Agilent 7890B) instrument with an HP-5 capillary column.

2.3 Catalytic tests

Methanol carbonylation experiments were performed in a continuous flow fixed-bed stainless steel reactor with 8 mm inner diameter. The flow of CO was controlled by means of a BROOKS mass flowmeter. Methanol was fed using a high-pressure constant flow pump or introduced by CO passing through a stainless steel saturator which was filled with methanol and placed in an electro-thermostatic water cabinet to provide the desired vapor pressure. All the reaction products were analyzed online using a gas chromatograph (Agilent 7890A) equipped with an HP-FFAP capillary column (30 m \times 530 μm \times 1.5 μm) connected to a flame ionization detector and a Porapak N capillary column connected to a thermal conductivity detector. 2.4 mL min^{-1} helium was used as the carrier gas in the capillary column. The gas chromatograph oven temperature was increased from 313 K to 373 K at a ramping rate of 10 K min^{-1} , then increased to 453 K at a ramping rate of 20 K min^{-1} , and finally held for 10 min. The conversion of methanol and the selectivities to products were calculated from the number of carbon atoms.

3 Results and discussion

3.1 Catalyst characterization results

X-ray diffraction (XRD) patterns (Fig. S1[†]) indicate that the crystal form and crystallinity are nearly the same after pyridine adsorption. Field-emission scanning electron microscopy (SEM) images (Fig. S2[†]) suggest that Py-MOR has a rod-like structure with a length of 2–5 μm and the morphology remains the same as that of H-MOR. Fourier transform infrared (FT-IR) spectra (Fig. S3[†]) prove that pyridine selectively adsorbs on Brønsted acid sites in 12-MR channels rather than in 8-MR channels of H-MOR.

3.2 Catalytic activity

Vapor-phase carbonylation of methanol was conducted at about 5.0 MPa with a 0.5% methanol–99.5% CO mixture at a weight hourly space velocity (WHSV) of 0.11 g (g catalyst)⁻¹ h⁻¹ (methanol) using the as-prepared Py-MOR catalyst. The effects of reaction temperature on methanol conversion and product selectivity of the Py-MOR catalyst are shown in Fig. 1a. At a lower reaction temperature (473 K), the methanol conversion is about 92% and DME is the predominant product with higher than 64% selectivity. With gradually increasing the temperature from 483 to 493 K, the methanol conversion continually increases and the MAc selectivity increases to higher than 59%. At a temperature higher than 503 K, the methanol conversion approaches 100% and almost no DME is produced. The HAc selectivity gradually increases with the increased reaction temperature from 473 to 543 K. At 543 K, the selectivity to HAc is about 95.3% with a MAc selectivity of about 2.7% and the weight ratio of water/HAc is less than 1% by calculation. Under all the reaction temperatures, the total selectivities to by-products, which primarily contain methyl formate, acetone and

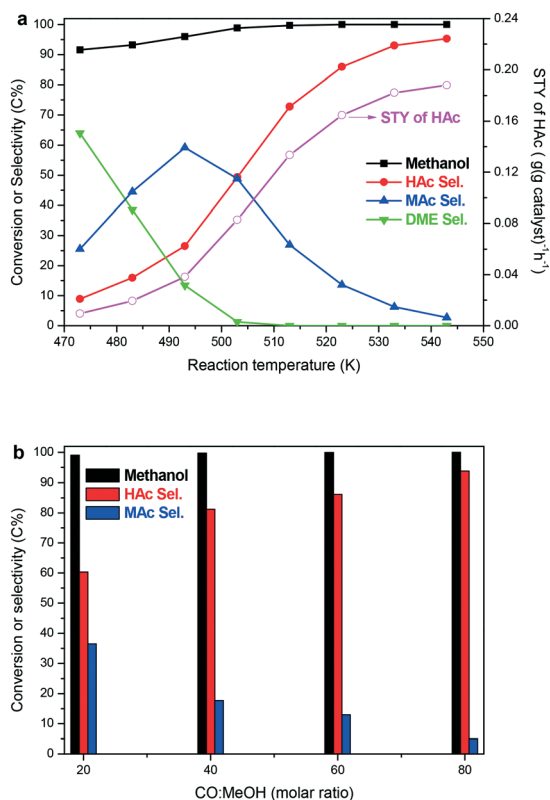


Fig. 1 Reaction performance. (a) Effects of reaction temperature on methanol conversion and product selectivity of the Py-MOR catalyst. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 200/1, and WHSV (methanol) = 0.11 g (g catalyst)⁻¹ h⁻¹. ■ Methanol conversion, ● HAc selectivity, ▲ MAc selectivity, ▼ DME selectivity, and ○ STY of HAc. (b) Effects of CO/methanol on methanol conversion and product selectivity of the Py-MOR catalyst. Conditions: reaction pressure = 5.0 MPa, WHSV (methanol) = 0.11 g (g catalyst)⁻¹ h⁻¹, and reaction temperature = 543 K. Black bar: Methanol conversion, red bar: HAc selectivity, and blue bar: MAc selectivity.

hydrocarbons, are less than 2%. The space time yield (STY) of HAc also gradually increases with increasing temperature and reaches about 0.2 g (g catalyst)⁻¹ h⁻¹ at 543 K. CO₂ is hardly detected in the products, because without the presence of a metal catalyst, the water gas shift reaction rate is very low. The efficiency of this type of catalyst can be improved *via* optimization of H-mordenite zeolites. It can be seen from Fig. S4† that the selectivity to and STY of HAc reach 96.8% and 0.4 g (g catalyst)⁻¹ h⁻¹ at 565 K, respectively.

The effects of CO/methanol molar ratios are also studied at 543 K and the results are shown in Fig. 1b. With the CO/methanol ratio decreasing from 80 to 20, the HAc selectivity decreases from 93.8 to 60.3%, whereas the MAc selectivity increases from 5.0 to 36.5%. The effects of reaction temperature on methanol conversion and product selectivity using the Py-MOR catalyst at CO/methanol = 20/1 are shown in Fig. S5.† The selectivity to and STY of HAc approach 94% and 0.25 h⁻¹ at 573 K, respectively. High selectivity to MAc can be obtained at lower reaction temperatures and lower CO/methanol molar ratios.

The carbonylation stability tests were conducted at 523 K and 5.0 MPa with a 0.25% methanol–99.75% CO mixture at a WHSV of 0.05 g (g catalyst)⁻¹ h⁻¹ (methanol). As shown in Fig. 2a, the activity of Py-MOR is very stable with about 100% methanol conversion; only little deactivation is observed; the HAc selectivity is higher than 90%; the selectivity to acetyl products (HAc and MAc) is about 98.5% during the 145 h reaction. For comparison, H-MOR was selected as a reference and the test was conducted under the same reaction conditions. As displayed in Fig. 2b, methanol is completely converted and the HAc selectivity is about 91% during the initial 4 h. Thereafter, the HAc selectivity rapidly drops to about 14% at 20 h, whereas the selectivity to MAc quickly increases and reaches a maximum (40%) at 15 h. Then, the MAc selectivity and methanol conversion slowly decrease. DME is first observed after 8 h of reaction and its selectivity increases with time on stream. After 30 h of reaction, the selectivities to HAc, MAc and DME remain about the same. Fig. S6† compares the catalytic stability of Py-MOR, H-MOR and Cu-MOR with 1.3% Cu content made by ion-exchange at lower methanol or derived DME conversion. Cu-MOR has been extensively studied in methanol or DME carbonylation because Cu species can activate CO and increase the rate of

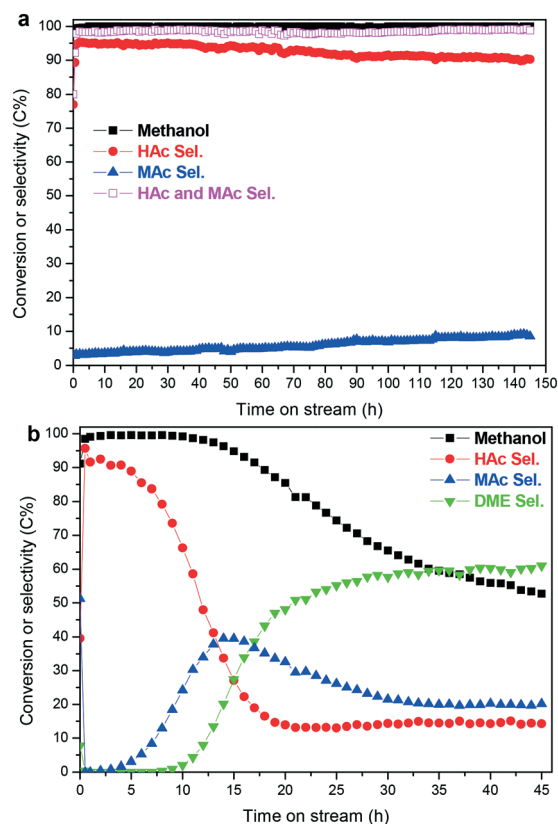


Fig. 2 Results of carbonylation stability tests. (a) Py-MOR. (b) H-MOR. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 400/1, WHSV (methanol) = 0.05 g (g catalyst)⁻¹ h⁻¹, and reaction temperature = 523 K. ■ Methanol conversion, ● HAc selectivity, ▲ MAc selectivity, ▼ DME selectivity, and □ HAc and MAc selectivity.

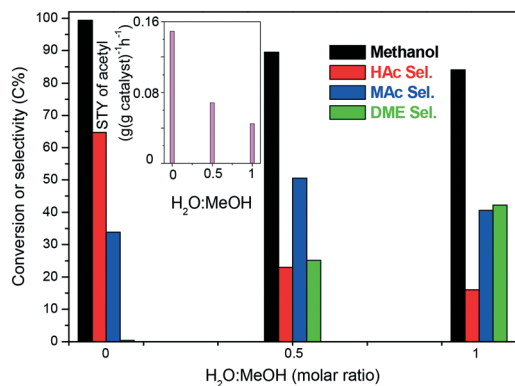


Fig. 3 Influence of water content on methanol conversion and product selectivity of the Py-MOR catalyst. Conditions: reaction pressure = 5.0 MPa, CO/methanol = 20/1, WHSV (methanol) = 0.15 g (g catalyst)⁻¹ h⁻¹, and reaction temperature = 543 K. Black bar: Methanol conversion, red bar: HAC selectivity, blue bar: MAc selectivity, green bar: DME selectivity, and magenta bar: STY of acetyl.

carbonylation.^{11,23} It is clear that the stability of Py-MOR is also much higher than those of H-MOR and Cu-MOR.

3.3 Influence of water

The influence of water content on methanol conversion and product selectivity of the Py-MOR catalyst is exhibited in Fig. 3. With the H₂O/methanol molar ratio increasing from very low to 1, the methanol conversion, HAC selectivity and acetyl (CH₃CO) STY decreased from 99.3%, 64.7% and 0.15 h⁻¹ to 84.0%, 16.0% and 0.04 h⁻¹, respectively. These reaction results evidently prove that the additional water in the reactant has a negative effect on methanol carbonylation to HAC, because the number of surface methoxy groups, which are formed by the reaction of methanol with Brønsted acid sites and further react with CO to produce acetyl, is reduced by competitive adsorption of water on these sites, which is in good accordance with previous theoretical calculations.¹⁴ For another reason, the 8-MR channels, which are the active sites for CO insertion into methoxy groups, might be blocked by [(CH₃)(H₂O)_n]⁺ clusters.¹⁷ As is known, the [(CH₃)(H₂O)_n]⁺ clusters will decompose with increasing the reaction temperature. Therefore, the competitive adsorption of methanol or H₂O on Brønsted acid sites is the key point. The STY of acetyl and the selectivity to HAC from methanol carbonylation operated at 543 K with a mixture of methanol and H₂O (H₂O/MeOH = 0.5) as a feed (Fig. 3) are nearly the same as those obtained at 523 K with pure methanol as a feed (Fig. S5†), which suggests that a higher reaction temperature is more effective for methanol competitive adsorption on the active sites in Py-MOR. Hence, the negative influence of H₂O can be solved by increasing the reaction temperature.

3.4 Coke analysis

The thermal decomposition behaviors of the catalysts are studied by thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses, and the results are shown

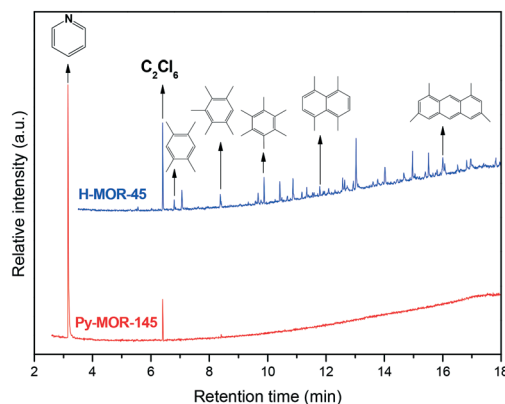


Fig. 4 GC-MS chromatograms of the organic materials retained in the catalysts after the reaction. C₂Cl₆ is used as the internal standard. Blue curve: H-MOR after the reaction for 45 h and red curve: Py-MOR after the reaction for 145 h.

in Fig. S7.† Fresh Py-MOR (as reference), used Py-MOR in Fig. 2a (Py-MOR-145) and used H-MOR in Fig. 2b (H-MOR-45) are 9.1, 10.0 and 12.4 wt%, respectively. H-MOR-45 shows a large peak at 838 K, which is due to the removal of hard coke-like polyaromatics,^{19,21} which results in the deactivation of H-MOR catalysts. Compared with the DTG peaks of fresh Py-MOR, the peak at 901 K for Py-MOR-145 may be primarily attributed to the adsorbed pyridine. H-MOR-45 and Py-MOR-145 were dissolved in HF and their soluble cokes were extracted with CH₂Cl₂ and analyzed by GC-MS. As displayed in Fig. 4, a large quantity of aromatic compounds (such as methylbenzenes and polycyclic aromatics), which are hardly detected in Py-MOR-145, exists in H-MOR-45. Methylbenzenes acceptably act as the “hydrocarbon pool” in zeolites,²⁸ which are beneficial to the methanol-to-hydrocarbon reaction. The molecular sizes of polycyclic aromatics are too large to inhibit the access to reactants and products. From the coke analysis above, it is concluded that the 12-MR channels of H-MOR are the locations for coking, and adsorption of pyridine in the 12-MR channels can effectively prevent the formation of cokes in methanol carbonylation to HAC.

Conclusions

In summary, a very stable, selective, halide-free, and noble metal-free pyridine-modified mordenite catalyst is developed for direct carbonylation of methanol to HAC. This catalyst can effectively solve the conflict that a low reaction temperature leads to a lower carbonylation rate due to the inhibition of adsorbed water, whereas a high reaction temperature causes rapid catalyst deactivation because of the higher coke formation rate. The methanol conversion, HAC selectivity, and STY of HAC can reach about 100%, 95% and 0.2 g (g catalyst)⁻¹ h⁻¹ at 543 K, respectively. Only little deactivation is observed during the 145 h reaction with higher than 90% HAC and about 98% acetyl product selectivities. It is suggested that this green process for producing HAC *via* direct carbonylation

of methanol on the Py-MOR catalyst is promising for industrial applications.

Conflicts of interest

There are no conflicts to declare.

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