Cite this article as: Chin J Catal, 2010, 31: 729-738.

Available online at www.sciencedirect.com

ScienceDirect

RESEARCH PAPER

Stability Enhancement of H-Mordenite in Dimethyl Ether Carbonylation to Methyl Acetate by Pre-adsorption of Pyridine

LIU Junlong¹, XUE Huifu¹, HUANG Xiumin¹, WU Pei-Hao², HUANG Shing-Jong³, LIU Shang-Bin^{2,*}, SHEN Wenjie^{1,#}

¹State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
 ²Institute of Atomic and Molecular Sciences, "Academia Sinica", Taipei 10617, Taiwan, China
 ³Department of Chemistry, Taiwan University, Taipei 10617, Taiwa, China

Abstract: The carbonylation of dimethyl ether to methyl acetate over H-mordenite (HMOR) and pyridine-modified HMOR was compared. The catalytic stability of HMOR was improved significantly by pyridine pre-adsorption, and a yield of methyl acetate ~30% was still obtained after 48 h on stream at 473 K. In situ infrared spectroscopy and ammonia temperature-programmed desorption revealed that pyridine preferentially occupied the acidic sites in 12-membered ring pores but not the acidic sites in 8-membered ring pores. ¹²⁹Xe NMR studies suggested that the channels of HMOR were blocked by coke in the reaction but those in the pyridine-modified HMOR were not. The acidic sites in the 12-membered ring pores were responsible for the deactivation of HMOR, and the reaction can be directed to occur mainly on the acidic sites in the 8-membered ring pores by the selective adsorption of pyridine in the 12-membered ring pores.

Key words: dimethyl ether; carbonylation; methyl acetate; H-mordenite; pyridine; stability

The present industrial production of acetic acid is mainly by methanol carbonylation in the Monsanto or BP CativaTM homogeneous processes, which use rhodium or iridium catalysts and methyl iodide as promoter [1]. Due to concerns over environmental pollution and production cost, the trend in recent methanol carbonylation is to avoid the use of corrosive halides and expensive precious metals and to rely on a heterogeneous process using solid acid catalysts [2-4]. For example, Y-type zeolites and sulfated zirconia catalysts have been investigated for the vapor phase carbonylation of methanol [2]. but the main product is dimethyl ether (DME) with only trace amounts of acetic acid and hydrocarbons at 473 K. Upon increasing the temperature to 573 K, the yield of hydrocarbons was increased, but the yield of acetic acid was increased only marginally. On the other hand, over H-ZSM-5 and H-mordenite (HMOR), acetic acid was formed with a yield of 0.4% at 473 K [2]. The catalytic performance of these zeolites could be improved by incorporating copper, which gave about

2% methyl acetyl yield at 523 K [2]. However, these solid acids suffered rapid deactivation by coking, especially at elevated temperatures [3]. Keggin polyoxometallate clusters containing Rh or Ir were also identified as active catalysts for methanol carbonylation with a methyl acetate yield of ca. 30% at 493 K, but this decreased to 16% when the methanol feed was replaced by DME [3–6]. Again, these catalysts were also found to form hydrocarbons, leading to severe deactivation by the deposition of carbonaceous residues.

Iglesia and co-workers [7–10] recently reported that HMOR and H-ferrierite (HFER) are good catalysts for the carbonylation of DME to methyl acetate (MA), and that HMOR is the more active and selective catalyst. A common feature of these two types of zeolites is the existence of 8-member ring (8-MR) channels, in which the reaction mainly occurs [9]. Kinetic and spectroscopic studies confirmed that the carbonylation of DME involves an interaction between the reactant and surface hydroxyl (–OH) groups on the zeolite catalyst to form methoxy

*Corresponding author. Tel: +886-2-2366-8230; Fax: +886-2-23620200; E-mail: sbliu@sinica.edu.tw

Received date: 24 December 2009.

^{*}Corresponding author. Tel: +86-411-84379085; Fax: +86-411-84694447; E-mail: shen98@dicp.ac.cn

Foundation item: Supported by the National Natural Science Foundation of China (20973166).

Copyright © 2010, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved. DOI: 10.1016/S1872-2067(09)60081-4

species, which was followed by the insertion of CO molecules to form acetyls in the rate-determining step. These acetyls further react with DME to produce MA and regenerate the surface methoxy species [7-9,11]. When DME was replaced by methanol, however, the reaction was slow due to the strong inhibition by water generated by methanol dehydration to DME. Theoretical calculations showed that the unique catalytic properties observed for these zeolites with 8-MR channels are due to the size of the pore where the active sites were located and also the unique orientation of the methoxy groups in the pore channels [12]. More importantly, the transition state during the insertion of CO into the methoxide fitted perfectly in the 8-MR channels. The negative effect of water on the carbonylation reaction rate was attributed to their strong adsorption on the acidic sites, which reduced available methoxy groups for CO.

These pioneering and fundamental studies give the reaction mechanism and role of the unique 8-MR channels in DME carbonylation. However, the stability of the HMOR catalyst, which is important to the industrial application of this process, was not much discussed. It is well known that the addition of a small amount of amine to the feedstream can significantly promote the selectivity in various processes by poisoning the strong framework Brönsted acid sites of the zeolites, e.g., in the epoxidation of cyclohexanol [13]. It should be noted that the addition of amine usually improved the selectivity of the reaction but decreased the catalytic activity considerably [14,15]. In this work, we report a procedure to improve the stability of HMOR while keeping a high MA yield during DME carbonvlation. This procedure was the use of the pre-adsorption of pyridine on HMOR, which led to preferential blocking of the acidic sites in the 12-MR pores while leaving the acidic sites in 8-MR pores undisturbed. Consequently, the pyridine-modified HMOR catalyst showed significantly enhanced stability for DME carbonylation with MA vield exceeding 30% for at least 48 h on stream at 473 K.

1 Experimental

1.1 Catalyst preparation

A commercially available Na-mordenite (NaMOR) with a Si/Al ratio of 6.4 and surface area of 434 m^2/g was used as the precursor. The HMOR sample was obtained from NaMOR by ion exchange. NaMOR (100 g) was dispersed in 1 L of NH₄NO₃ aqueous solution (1 mol/L) at 353 K for 3 h followed by filtration and washing with distilled water. After repeating the ion exchange three times, the resulting solid was dried at 383 K for 12 h and then calcined at 773 K for 6 h in air, which yielded the HMOR-6 catalyst. In order to adjust the Si/Al ratio, the HMOR-6 sample was then treated with a 2 mol/L HNO₃ solution (40 ml/g) at 373 K for 10 h followed by drying at 383 K for 12 h and calcination at 773 K for 6 h in air. This proce-

dure yielded a HMOR-10 catalyst with a Si/Al ratio of 9.6.

To prepare the pyridine-modified catalysts, 600 mg HMOR (40–60 mesh) was loaded into a stainless steel fixed-bed reactor (8 mm i.d.), heated to 773 K at a rate of 10 K/min under N₂ flow (30 ml/min), and maintained at this temperature for 1 h. After cooling to 573 K, the sample was purged with a 1.3% pyridine-98.7% N₂ mixture (30 ml/min) for 1 h and then flushed with N₂ (30 ml/min) for 1 h, which yielded the Py-HMOR catalysts.

1.2 Catalyst characterization

Field-emission scanning electron microscopy (FESEM) images were recorded using a Philips Fei Quanta 200F instrument operated at 20 kV. The samples were placed on a conductive carbon tape on an aluminum sample holder.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector-22 instrument with a resolution of 2 cm^{-1} . The samples were pressed into a self-supporting wafer and evacuated $(2 \times 10^{-2} \text{ Pa})$ in the IR cell at 723 K for 5 h. Adsorption of pyridine was conducted at 298-573 K for 5 min to ensure a saturated loading prior to the acquisition of the IR spectrum at room temperature. All spectra were normalized using the overtone and combination vibrations of HMOR zeolite at 1 876 and 1 985 cm⁻¹. In situ IR spectra were obtained using a high temperature and pressure cell. The sample was pressed into a self-supporting disk and mounted into the cell. It was then purged with He at 723 K for 4 h. The adsorption of MA was conducted at room temperature, and the catalyst sample was then heated in a He flow. DME carbonylation was performed by introducing a 5% DME-50% CO-2.5% N2-42.5% He mixture at 473 K with the cell pressurized to 1.0 MPa. Spectra were then recorded as a function of reaction time.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out using a U-shape quartz tube reactor on a chemisorption apparatus (AutoChem II 2920). For each run, 100 mg sample was heated to 473 K at a rate of 10 K/min, maintained at the this temperature for 1 h under N₂ flow (30 ml/min), and then purged with a 10% NH₃-90% He gas mixture (30 ml/min) at 473 K for 30 min. Subsequently, physisorbed ammonia was removed by purging the sample with a 0.6% H₂O-99.4% N₂ mixture (30 ml/min) at 473 K for 1 h. After cooling to room temperature, the sample was heated to 873 K at a rate of 10 K/min under He flow (20 ml/min). The outlet gas was collected after passing through a solid KOH trap to remove water and a dry ice trap to trap pyridine. The amount of desorbed NH₃ was then measured by a thermal conductivity detector (TCD).

¹²⁹Xe NMR spectra of xenon adsorption on the samples were recorded on a Bruker Avance-300 instrument operated at a Larmor frequency of 83.012 MHz using a single pulse sequence with a $\pi/2$ pulse of 15 µs and a recycle delay of 2 s. Typically, 128 000 free induction delay signals were accumu-

lated for each spectrum. Diluted Xe gas was used as the chemical shift reference. The details of the experimental procedure can be found elsewhere [16].

Temperature-programmed oxidation (TPO) measurements of the samples were conducted with a U-shape micro-reactor connected to a mass spectrometer (QMS-200, Omnistar). Before the experiment, the sample (100 mg) was pre-treated at 473 K for 1 h under He flow (40 ml/min). After cooling to room temperature, the sample was heated to 1 073 K at a rate of 10 K/min in a flowing 20% O₂-80% He mixture (60 ml/min). The effluent was monitored by a mass spectrometer.

1.3 Catalytic test

DME carbonylation was conducted with a continuous flow fixed-bed stainless steel reactor. In the case of HMOR, 600 mg of catalyst (40–60 mesh) was loaded into the reactor, heated to 773 K at a rate of 10 K/min under N₂ flow (30 ml/min) and maintained at this temperature for 1 h. After the catalyst sample was cooled to 473 K, a 5% DME-50% CO-2.5% N₂-42.5% He mixture was introduced at a gas hourly space velocity (GHSV) of 1 250 ml/(g·h) and the reactor was pressurized to 1.0 MPa. The effluent was analyzed by an online gas chromatograph (Agilent 6890N) equipped with a TCD and a flame ionization detector (FID). N₂ was used as an internal standard.

Similar reaction conditions were applied to the Py-HMOR catalysts. The HMOR was initially heated at 773 K under N_2

flow for 1 h. After cooled to 573 K, the sample was purged with a 1.3% pyridine-98.7% N₂ mixture (30 ml/min) for 1 h, and then flushed with N₂ for another 1 h before carrying out the DME carbonylation test.

2 Results and discussion

2.1 DME carbonylation

Figure 1(a) compares the conversions of DME and product selectivities during DME carbonylation over the HMOR-6 and Py-HMOR-6 catalysts as a function of time on stream (TOS). For the HMOR-6 catalyst, an induction period of 2.5 h was observed during which the conversion of DME reached 37%. The conversion of DME was maintained at this level for an additional 2.5 h, followed by a rapid deactivation to a conversion of DME of only 6% at 18 h on stream. The selectivity for MA was more than 98% for about 5 h, but it rapidly decreased to only 50% at 18 h on stream. On the other hand, the selectivities for methanol and hydrocarbons (HCs) were practically zero during the initial stage, but they increased significantly to 35% and 14%, respectively, at 18 h on stream. This reaction pattern indicated that the typical HMOR lost activity due to coking during the course of reaction and that the deposition of carbonaceous residues (cokes) in the pore channels inhibited the formation of MA but promoted the formation of significant amounts of methanol and hydrocarbons.



Fig. 1. Conversion of DME and selectivities for MA, methanol, and HCs during DME carbonylation over the HMOR-6 and Py-HMOR-6 catalysts (a) and HMOR-10 and Py-HMOR-10 catalysts (b). Reaction conditions: 473 K, 5% DME-50% CO-2.5% N₂-42.5% He, 1250 ml/(g·h), 1.0 MPa.

For the Pv-HMOR-6 catalyst, an increased induction period to 11 h was observed. The conversion of DME gradually increased to 33% and was maintained at this level for 48 h on stream without deactivation. The selectivity for MA increased from 90% in the initial stage to a plateau value of 99% while the selectivity for methanol decreased progressively from 10% in the initial stage to less than 1% at extended TOS. Interestingly, unlike over the HMOR-6 catalyst, there was no detectable formation of hydrocarbons over the Py-HMOR-6 catalyst. Apparently, the pre-treatment by the adsorption of pyridine significantly enhanced the stability of HMOR during DME carbonylation. Long-term stability test further revealed that a rather stable performance was obtained over the Py-HMOR-6 catalyst with MA selectivity of more than 99% while the conversion of DME only slightly decreased from 33% to 20% after 250 h on stream.

It was previously proposed that DME reacts with the Brönsted acid sites of HMOR during the induction period to form surface methoxy species and methanol, followed by the insertion of CO into the C-O bond of the tertiary surface-bound methyl to produce acetyl [7-9]. This reaction intermediate then reacted with DME to produce methyl acetate while regenerating a surface methyl group to complete the catalytic cycle. As a result, MA was formed as the sole product at steady state, typically with a superior selectivity of more than 99%. However, over the HMOR-6 catalyst, both the conversion of DME and selectivity for MA declined significantly after 5 h on stream, whereas the selectivity for methanol increased to 35% due to the rapid deactivation by coking. Presumably, the significant amounts of water produced together with hydrocarbons led to the hydration of DME to methanol. In this context, the Py-HMOR-6 catalyst exhibited a better catalytic performance and stability than the HMOR-6, which indicated that the pre-adsorption of pyridine effectively inactivated the acidic sites in the 12-MR pore channels and left the acidic sites in the 8-MR pores as the active sites for DME carbonylation. However, the induction period was prolonged over Py-HMOR-6 because of the diffusion limitation of pyridine adsorption in the large channels.

Similar reaction patterns were observed on the HMOR-10 and Py-HMOR-10 catalysts except for their lower DME conversions, as illustrated in Fig. 1(b). Over the HMOR-10 catalyst, the conversion of DME approached 16% during the induction period of about 3 h. It was maintained at this level for 4 h followed by a rapid deactivation with the formation of significant amounts of methanol and HCs. However, this deactivation rate was much lower than that over the HMOR-6 catalyst, and the conversion of DME only decreased to 9% after 18 h on stream. Again, the Py-HMOR-10 catalyst exhibited considerably enhanced stability. The conversion of DME gradually increased to about 13% during the induction period of 13 h and it was maintained at this level for 50 h on stream. MA was produced as the main product with a selectivity of 99% while the selectivity for methanol was less than 1%. Apparently, acidic leaching (dealumination) of the HMOR-6 sample decreased the Brönsted acid sites in the 8-MR channels and caused a remarkable loss in activity. Simultaneously, it also eliminated the acidic sites in the 12-MR channels, which gave a slow deactivation rate. For the two HMOR samples with different Si/Al ratios, pyridine pre-adsorption in the 12-MR pores significantly improved the stability during DME carbonylation. However, although it caused diffusion limitation of the reactants and products as indicated by the extended induction period.

2.2 FESEM and NH₃-TPD

Figure 2 shows the FESEM images of the HMOR and Py-HMOR catalysts. The HMOR-6 sample exhibited a traditional block-like morphology with the size of \sim 5 µm in length



Fig. 2. FESEM images of the HMOR-6 (a, b), Py-HMOR-6 (c, d), HMOR-10 (e, f), and Py-HMOR-10 (g, h) samples.

and ~1 μ m in width. However, the size of Py-HMOR-6 was shortened to 1–3 μ m and the morphology became relatively irregular. For the HMOR-10 sample, the original block-like morphology of the parent zeolite was partly destroyed by the acid leaching treatment and the average length was decreased to ~4 μ m. Similarly, the average size of the Py-HMOR-10 catalyst was further shortened to ~2 μ m after pyridine adsorption at 573 K.

Mordenite has a two-dimensional framework structure consisting of straight 12-MR pore channels (0.67 \times 0.70 nm) connected by twisted $(0.28 \times 0.57 \text{ nm}, \text{ side pockets along } (001)$ crystal facet) and crossed $(0.34 \times 0.48 \text{ nm}, \text{ along } (010) \text{ crystal}$ facet) 8-MR pores [17]. It is a common practice to measure the overall acidity of HMOR by FT-IR, NMR, and NH3-TPD techniques [9,18,19], but the discrimination and quantitative determination of the acidic sites in the 12-MR and the 8-MR pores still remain a challenging task. As illustrated in Fig. 3, the NH₃-TPD profile of HMOR-6 exhibited two NH₃ desorption peaks centered at 497 and 826 K, corresponding to weak and strong acid sites, respectively. However, the weakly adsorbed ammonia can be effectively removed by a water treatment, facilitating the quantitative determination of the strong protonic acid sites [19]. Accordingly, the amount of Brönsted acid sites in the HMOR-6 catalyst was estimated to be 1.01 mmol/g, while it was only 0.69 mmol/g in the HMOR-10 sample due to dealumination (Table 1).



Fig. 3. NH_3 -TPD profiles of HMOR-6 before (1) and after (2) treatment with a 0.6% H₂O-99.4% N₂ mixture for 1 h, and HMOR-10 (3), Py-HMOR-6 (4), and Py-HMOR-10 (5).

For the Py-HMOR samples, similar NH₃-TPD profiles to those of the HMOR samples were observed with nearly the same desorption temperature for the strong acid sites, but the acid amounts were only 0.52 and 0.30 mmol/g for the Py-HMOR-6 and Py-HMOR-10 catalysts, respectively. This indicated that the amount of Brönsted acidity presented in the 8-MR pores was 52% of the total acid concentration in HMOR-6, which is in good agreement with the result (55%) estimated by IR spectroscopy [9]. In the case of Py-HMOR-10, the acid amount in the 8-MR pores was 43% of the total amount in HMOR-10. This difference may be due to the decreased crystallinity (91%) of HMOR-10 because of the acid leaching treatment. Probably, pyridine has partial access to the 8-MR pores [20].

Because the size of pyridine (kinetic diameter 0.585 nm) is similar to the size of the 12-MR channels but much larger than the size of the 8-MR channels, pyridine is selectively adsorbed on the acidic sites located in the 12-MR channels during the pre-adsorption at 573 K, but not on those in the 8-MR channels. Consequently, the Brönsted acid sites in the 12-MR pores were effectively passivated by pyridine adsorption, and DME carbonylation occurred preferentially in the 8-MR pores, leading to a superior catalytic stability compared to the parent HMOR samples. Based on the amount of the acidic sites in the 8-MR pores, the turnover frequency (TOF) of DME carbonylation on the HMOR-6 sample was estimated to be 1.9 h^{-1} , while it was marginally decreased to 1.8 h^{-1} on the Pv-HMOR-6 catalyst (Table 1). Similarly, the TOF was 1.5 h^{-1} over the HMOR-10 catalyst and it was decreased to 1.3 h^{-1} on the Py-MOR-10 catalyst. These results are clear evidence that the acidic sites in the 8-MR pores are the active centers for DME carbonylation, and the small variation in the TOFs may be due to the diffusion limitation of pyridine adsorption in the 12-MR pores.

2.3 FT-IR spectra

Figure 4(a) shows the FT-IR spectra of the catalysts in -OH stretching and pyridine vibration regions. There are three bands in the OH stretching region: two broad bands at 3 740 and 3 656 cm⁻¹ and one asymmetric sharp band at 3 616 cm⁻¹ for the HMOR samples. The band at 3 740 cm⁻¹ was assigned to Si–OH and it became intense with the HMOR-10 sample because of the creation of more terminal Si-OH on the framework upon dealumination. The band at 3 656 cm⁻¹ was attrib-

Table 1	Characteristics and a	activity of the HMOR	catalysts
---------	-----------------------	----------------------	-----------

Catalyst	Relative crystallinity ^a (%)	Si/Al ratio ^b	NH ₃ desorption amount (mmol/g)	DME carbonylation TOF (h ⁻¹)
HMOR-6	100	6.4	1.01	1.9
Py-HMOR-6	—	6.4	0.52	1.8
HMOR-10	91	9.6	0.69	1.5
Py-HMOR-10	—	9.6	0.30	1.3

^aXRD analysis; ^bXRF analysis.



Fig. 4. FT-IR spectra in the –OH stretching region of HMOR-6 (1), HMOR-10 (3), pyridine saturation and evacuation at 573 K (2, 4) and their subtractions (a); Pyridine adsorption over HMOR-6 (b) and HMOR-10 (c) at 298 K (1), 473 K (2), 573 K (3), evacuated at 573 K (4) and after 48 h DME carbonylation reaction (5).

uted to non-framework Al–OH moieties. The decrease in the intensity of this band in the HMOR-10 sample indicated that the acidic treatment has partially removed the non-framework aluminum species. The band at 3 616 cm⁻¹ assigned to acidic bridging OH also decreased significantly for the HMOR-10 sample. This was because the acidic leaching caused the cleavage of framework aluminum and thus removed the acidic OH groups and simultaneously created more terminal Si–OH species.

The intensity of the band at 3 616 cm⁻¹ decreased considerably and a new band at 3 595 cm⁻¹ was seen for the Py-HMOR samples. This can be seen by subtracting the spectra of the pyridine-adsorbed samples from the parent HMOR samples. Because the bands at 3 616 and 3 595 cm⁻¹ were due to the Brönsted acid sites in the 12-MR pores and the 8-MR pores [21–23], the remarkably decreased intensity of the band at 3 616 cm⁻¹ indicated that pyridine was mainly adsorbed on the acidic sites in the 12-MR pores, while the acidic sites in the 8-MR pores was almost inaccessible to pyridine.

Upon adsorption of pyridine on the HMOR-6 sample at room temperature, typical absorption bands assigned to Brönsted acid sites (1 550 cm⁻¹) and Lewis acid sites (1 455 cm⁻¹) appeared. The band at 1 492 cm^{-1} is usually attributed to the vibrations of pyridine adsorbed on both the Brönsted and Lewis acidic sites [24]. The intensities of these characteristic bands increased with increasing of the temperature of pyridine adsorption and reached their maxima at 573 K. The band responsible for Brönsted acidity became more pronounced upon adsorption of pyridine at 473 K. On the other hand, the adsorption of pyridine on the Lewis acidic sites (i.e., the band at 1 455 cm⁻¹) was saturated below 473 K. These observations imply that a saturated adsorption of pyridine on HMOR-6 can readily be achieved at 573 K. In addition, other two bands at 1 638 and 1 620 cm⁻¹ further confirmed the saturated adsorption of pyridine on the HMOR-6 at 573 K. The former is usually assigned to pyridine adsorbed on Brönsted acid sites (PyH⁺), whereas the latter is due to pyridine adsorbed on both Brönsted and Lewis acid sites (LPy) [25]. Meanwhile, a weak band at 1 448 cm⁻¹ appeared upon pyridine adsorption at room temperature, but it almost entirely disappeared on evacuation at 573 K. This weak band is usually assigned to physically adsorbed pyridine on Si–OH [25]. A similar pyridine adsorption behavior on the HMOR-10 sample was observed, but the band at 1 448 cm⁻¹ was relatively more intense due to the creation of more Si–OH groups by dealumination. Again, the intensity of the band at 1 550 cm⁻¹ due to the Brönsted acid sites increased with increasing adsorption temperature and it reached its maximum at 573 K. The intensity of the band at 1 455 cm⁻¹ assigned to the Lewis acid sites varied only slightly with temperature, indicating that the Lewis acid sites were readily saturated by pyridine adsorption at lower temperatures.

Over the 48 h reacted Py-HMOR catalysts, adsorption bands assigned to multi-methyl pyridine (1 640, 1 508, and 1 494 cm⁻¹) were observed, which indicated that pyridine adsorbed on the Brönsted acid site reacted with DME or adsorbed methyl to form new adsorbed species during carbonylation.

Figure 5 shows the FT-IR spectra of MA and CO/DME adsorption on the HMOR-6 catalyst. Pure MA exhibited bands at 1 783, 1 756, 1 449, and 1 378 cm⁻¹ due to the vibrations of v_{as} (C=O), v_{a} (C=O), δ_{as} (CH), and δ_{a} (CH), respectively. Upon adsorption on the HMOR-6 catalyst at room temperature, weakly adsorbed MA with the characteristic bands at 1 783 and 1 756 cm⁻¹ and strongly adsorbed MA on the Brönsted acid sites with the typical bands at 1 720 and 1 700 cm⁻¹ were observed. When the sample was heated to 373 K, the weakly adsorbed MA was entirely desorbed as confirmed by the disappearance of the bands at 1 783 and 1 756 cm⁻¹, and the strongly adsorbed MA was partially desorbed as seen by the considerable decrease in the intensities of the bands at 1 720 and 1 700 cm⁻¹.

When the 5% DME-50% CO-2.5% N_2 -42.5% He mixture was introduced into the IR cell at 473 K, a typical band at 1 454



Fig. 5. FT-IR spectra of MA adsorption (a) and DME carbonylation on the HMOR-6 catalyst (b).

cm⁻¹ for DME adsorption was observed during the initial 30 min. Significant amounts of methyl acetate were produced at 1 h as indicated by the appearance of the bands at 1 783, 1 756, and 1 378 cm⁻¹. Simultaneously, the band at 1 705 cm⁻¹ representing v(C=O) of the acetyl-zeolite intermediate appeared and its intensity gradually became prominent with reaction time to 10 h [26]. This confirmed that surface methyl and acetyl were the major intermediates in DME carbonylation.

2.4 ¹²⁹Xe NMR

¹²⁹Xe NMR of adsorbed xenon was used to explore the porosity of the HMOR-6 samples before and after adsorption of pyridine. Figure 6 shows the ¹²⁹Xe NMR spectra of HMOR-6 with different Xe loading. All spectra exhibited slightly asymmetric lineshapes and can be deconvoluted into two separate peaks. The peak with a lower chemical shift, which



Fig. 6. 129 Xe NMR spectra of Xe adsorbed on the HMOR-6 sample at various Xe partial pressures. 1 Torr = 133.3 Pa.

 Table 2
 ¹²⁹Xe NMR chemical shifts and relative areas obtained from the HMOR-6 samples

Same la	Xe pressure	Chemical sh	Chemical shift/Area (%)	
Sample	(Torr)	12-MR	8-MR	
HMOR-6	100	164/79	210/21	
	300	165/90	209/10	
	500	170/91	210/9	
	900	175/95	210/5	
Spent HMOR-6	300	176/3	214/97	
Py-HMOR-6	300	169/4	210/96	
Spent Py-HMOR-6	300	169/11	210/89	

increased linearly with Xe loading due to increased Xe-Xe interactions, was due to Xe adsorbed in the 12-MR pores [27,28]. The peak with the higher chemical shift, which was invariant with Xe pressure, was due to Xe adsorption in the 8-MR pores. Because the size of the Xe molecule (kinetic diameter 0.44 nm) is comparable to the aperture of the 8-MR pores, it is possible that the migration of Xe within the pores is by single file diffusion. As summarized in Table 2, upon increasing the Xe partial pressure from 100 to 900 Torr, the ¹²⁹Xe chemical shift due to Xe adsorbed in the 12-MR pores increased from $\delta = 164$ to 175, and the relative peak area also increased from 79% to 95%. Meanwhile, the chemical shift due to Xe in the 8-MR pores at ca. $\delta = 210$ remained practically unchanged with Xe pressure but its relative area decreased from 21% to 5%. This indicated that Xe tends to adsorb preferentially in the 8-MR over the 12-MR pores at low Xe loading, but there was a fast exchange between the two types of pores at high Xe loading [29,30].

Figure 7 displays the ¹²⁹Xe NMR spectra obtained from the fresh and spent samples at Xe partial pressure of 300 Torr. For the fresh HMOR-6, two resonance peaks at $\delta = 165$ and 209 with relative areas of 90% and 10% can be assigned to Xe adsorbed in the 12-MR and 8-MR pores, respectively. For the fresh Py-HMOR-6 sample obtained by pyridine adsorption at 573 K, the spectrum can be deconvoluted into two peaks centered at $\delta = 169$ and 210, and their relative areas were 4% and 96%, respectively. The slight increase in chemical shift (from δ = 165 to 169) of the peak corresponding to Xe adsorbed in the 12-MR pores can be attributed to interactions between Xe and adsorbed pyridine in addition to Xe-wall and Xe-Xe interactions. The peak area drastically decreased from 90% for HMOR-6 to only 4% for Py-HMOR-6, which indicated that adsorbed pyridine in HMOR-6 occupied the 12-MR pores, and thus forced the Xe to adsorb predominately in the 8-MR pores. As a result, the peak area responsible for Xe in the 8-MR pores increased from 10% to 96%. In addition to the weak gaseous Xe peak at $\delta = 0$, an additional broader resonance centered at ca. $\delta = 6$ was also observed for the Py-HMOR-6 sample. This weak peak may be attributed to Xe adsorbed in the inter-particle voids of the sample.

Compared to fresh HMOR-6, the spectrum of spent



Fig. 7. ¹²⁹Xe NMR spectra of Xe (pressure 300 Torr) adsorbed on HMOR-6 (1), spent HMOR-6 (2), Py-HMOR-6 (3), and spent Py-HMOR-6 (4).

HMOR-6 after DME carbonylation reaction for 18 h showed much broader asymmetric resonances centered at $\delta = 176$ and 214 with relative areas of 3% and 97%, respectively. The apparent shift of the two resonances toward high field is most likely due to the formation of carbonaceous compounds during the course of reaction. In this context, coke tended to preferentially deposit in the 12-MR pores, leading to a nearly complete blockage of the pore voids. It can be hypothesized that some of these carbonaceous deposits may also be located near the pore opening of the 8-MR pores, leading to partial blockage and hence the notable broadening and high-field shift of the resonance peak. These observations are in line with the rapid decrease in DME conversion after 5 h on stream (Fig. 1). On the other hand, a rather similar ¹²⁹Xe spectrum was observed for the fresh and spent Py-HMOR-6 catalysts, except for minor variations in the peak areas for Xe adsorbed in the 12-MR and 8-MR pores. This indicated that adsorption of pyridine in the 12-MR pores not only readily inhibited the formation of coke but also caused DME carbonvlation to occur selectively in the 8-MR pores, leading to a more stable catalytic performance.

2.5 TPO

Figure 8 shows the TPO profiles of the spent HMOR-6 samples at different stages of DME carbonylation. When used for 2 h, desorption of carbon oxides from 550 to 850 K was observed. A relatively strong desorption peak at ca. 600 K and a weak one at 800 K were seen, indicating that there were at least two types of coke species on the catalyst. The low temperature peak should be related to desorption of soft cokes, whereas the high temperature peak is due to hard cokes (polyaromatics) [31,32]. With reaction time, the intensity of the low temperature peak was unchanged, but the high temperature



Fig. 8. TPO profiles of the spent HMOR samples at different stages of DME carbonylation.

peak was more intense, indicating that severe deposition of hard coke has occurred during the course of reaction. The total amounts of carbon oxides desorbed gradually increased from 0.6 mmol/g at 2 h to 1.8 mmol/g at 10 h, but it sharply increased to 4.5 mmol/g at 15 h and then slowly approached 5.2 mmol/g at 24 h. Together with these hydrocarbons, amounts of methane and trace amounts of ethylene and propylene were formed during the deactivation process, as illustrated by the reaction pattern (Fig. 1).

In order to distinguish the type of coke, TPO measurements of the HMOR-6 sample with pre-adsorption of DME, MA, benzene, toluene, and trimethylbenzene at 473 K were performed. The results are shown in Fig. 9. Because the adsorption of DME and MA on the HMOR-6 catalyst produces surface bound methyl and acetyl groups as characterized by the



Fig. 9. TPO profiles of DME (1), MA (2), benzene (3), toluene (4), and trimethylbenzene (5) pre-adsorbed on the HMOR-6 samples.

FT-IR measurements, the desorption of carbon oxides at about 600 K can be attributed to these reaction intermediates. For the adsorption of benzene, toluene, and trimethylbenzene, the desorption of carbon oxides at 800 K was obviously due to the combustion of these compounds.

Therefore, the low temperature peak in the spent HMOR-6 sample at about 600 K was mainly due to the reaction intermediates, that is, surface bonded methyl species and deposits associated with the formation of hydrocarbons. The high temperature peak at about 800 K was associated with hard coke that block the 12-MR pores and hindered the diffusion of reactants and products, leading to severe deactivation. Considering the sizes of the main 12-MR (0.67 nm \times 0.70 nm) and the side 8-MR (0.28 nm \times 0.57 nm) pores, it is possible that the hard coke formed in the large 12-MR pores mainly consist of polyaromatics because the 8-MR pores are too small to accommodate even a benzene molecule (0.5 nm \times 0.70 nm). Moreover, the generation of water accompanied by the formation of hard coke and hydrocarbons caused the hydration of DME to produce significant amounts of methanol during the deactivation period.

Two main desorption peaks of carbon oxides were also detected for the spent Py-HMOR-6 catalyst (Fig. 1), but the desorption temperatures were shifted to higher regions (723 and 860 K, Fig. 10). By comparing the TPO profile obtained from the fresh Py-HMOR sample, the intense high temperature peak can be unambiguously assigned to the oxidation of adsorbed pyridine in the spent Py-HMOR-6 catalyst. Presumably, adsorbed pyridine in the 12-MR pores hindered the diffusion of oxygen, causing the desorption peak shift towards higher temperature. The weaker low temperature peak at 723 K might be due to the combustion of soft coke analogous to that observed for the spent HMOR-6 catalyst. Quantitative analyses revealed that the coke deposition rates were 314 and 32 umol/(g·h) for the HMOR-6 and Py-HMOR-6 catalysts, respectively, confirming the essential improvement in the stability of the Py-HMOR catalyst.



Fig. 10. TPO profiles of the fresh and spent Py-HMOR-6 catalysts.

3 Conclusions

Pre-adsorption of pyridine on HMOR improved its catalytic stability for DME carbonylation to methyl acetate. Adsorbed pyridine preferentially passivated the acidic sites in the 12-MR pores of HMOR but could not access the acidic sites in the 8-MR pores. Thus, DME carbonylation was directed to occur mainly in the 8-MR pores of the Py-HMOR catalyst, which led to the effective inhibition of coke formation and superior catalytic stability.

References

- 1 Sunley G J, Watson D J. Catal Today, 2000, 58: 293
- 2 Fujimoto K, Shikada T, Omata K, Tominnaga H. Chem Lett, 1984: 2047
- 3 Ellis B, Howard M J, Joyner R W, Reddy K N, Padley M B, Smith W J. *Stud Surf Sci Catal*, 1996, **101**: 771
- 4 Wegman R W. J Chem Soc, Chem Commun, 1994: 947
- 5 Volkova G G, Plyasova L M, Salanov A N, Kutova G N, Yurieva T M, Likholobov V A. *Catal Lett*, 2002, 80: 175
- 6 Volkova G G, Plyasova L M, Shkuratova L N, Budneva A A, Paukshtis E A, Timofeeva M N, Likholobov V A. *Stud Surf Sci Catal*, 2004, **147**: 403
- 7 Cheung P, Bhan A, Sunley G J, Iglesia E. Angew Chem, Int Ed, 2006, 45: 1617
- 8 Cheung P, Bhan A, Sunley G J, Law D J, Iglesia E. J Catal, 2007, 245: 110
- 9 Bhan A, Allian A D, Sunley G J, Law D J, Iglesia E. J Am Chem Soc, 2007, 129: 4919
- 10 Blasco T, Boronat M, Concepcion P, Corma A, Law D, Vidal-Moya J A. Angew Chem, Int Ed, 2007, 46: 3938
- 11 Jiang Y, Hunger M, Wang W. J Am Chem Soc, 2006, 128: 11679
- 12 Boronat M, Martinez-Sanchez C, Law D, Corma A. J Am Chem Soc, 2008, 130: 16316
- 13 Beck C, Mallat T, Bürgi T, Baiker A. J Catal, 2001, 204: 428
- 14 Müller C A, Schneider M, Mallat T, Baiker A. Appl Catal A, 2000, 201: 253
- 15 Corma A, Esteve P, Martínez A. J Catal, 1996, 161: 11
- 16 Fang L Y, Liu S B, Wang I. J Catal, 1999, 185: 33
- 17 Sano T, Wakabayashi S, Oumi Y, Uozumi T. Microporous Mesoporous Mater, 2001, 46: 67
- 18 Makarova M A, Wilson A E, Van Liemt B J, Mesters C M A M, De Winter A W, Williams C. *J Catal*, 1997, **172**: 170
- 19 Bagnasco G. J Catal, 1996, 159: 249
- 20 Viswanadham N, Kumar M. Microporous Mesoporous Mater, 2006, 92: 31
- 21 Zholobenko V L, Makarova M A, Dwyer J. J Phys Chem, 1993, 97: 5962
- 22 Eder F, Stockenhuber M, Lercher J A. J Phys Chem B, 1997, 101: 5414
- 23 Maache M, Janin A, Lavalley J C, Benazzi E. Zeolites, 1995, 15: 507
- 24 Auroux A, Datka J. Appl Catal A, 1997, 165: 473
- 25 Buzzoni R, Bordiga S, Ricchiard G, Lamberti C, Zecchina A,

Bellussi G. Langmuir, 1996, 12: 930

- 26 Kresnawahjuesa O, Gorte R J, White D. J Mol Catal A, 2004, 208: 175
- 27 Springuel-Huet M A, Fraissard J P. Zeolites, 1992, 12: 841
- 28 Pradhan A R, Wu J F, Jong S J, Chen W H, Tsai T C, Liu S B. Appl Catal A, 1997, 159: 187
- 29 Yang J H, Clark L A, Ray G J, Kim Y J, Du H, Snurr R Q. *J Phys Chem B*, 2001, **105**: 4698
- 30 Yuvaraj S, Chang T H, Yeh C T. J Catal, 2004, 221: 466
- 31 Palumbo L, Bonino F, Beato P, Bjorgen M, Zecchina A, Bordiga S. J Phys Chem C, 2008, 112: 9710
- 32 Guisnet M, Magnoux P. Appl Catal A, 2001, 212: 83