



In situ DRIFT study of dimethyl ether carbonylation to methyl acetate on H-mordenite



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ABSTRACT

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to study the reaction of dimethyl ether (DME) carbonylation to methyl acetate (MAc). Methoxyl and acetyl groups were observed in situ, confirming the reaction mechanistic proposal. DME adsorption bands on Si—OH, Al—OH and SiOHAl (Brønsted acid sites) groups were identified respectively. The effect of temperature and pressure on acetyl formation and side reactions were systematically studied. It was found that methoxyls formed by DME chemisorbed on Brønsted acid sites could be observed above 433 K. High pressure and appropriate temperature interval promoted the formation of acetyls. Side reactions, DME transformed into olefins and then into cokes, were favored at low pressure and high temperature. Carbonylation reactions on catalysts with acid sites only in 8MR side pockets and 12MR main channels of mordenite (samples noted as HMOR-SP and HMOR-MC) were conducted by in situ DRIFT spectroscopy and catalytic testing. Pyridine molecules adsorbed in 12MR main channels resulted in the low utilization of acid sites in 8MR side pockets. The synthesis rate of MAc on HMOR-SP was stable but lower. HMOR-MC presented the lowest MAc synthesis rate with the production of coke, which was also observed in DRIFT spectra.

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1. Introduction

Ethanol, one of the most important renewable fuels, can be used as fuel additive, hydrogen carrier, chemical feedstock, and so on. The production and transformation of ethanol have been triggering wide research interest [1–4]. Traditional commercialized route by hydration of ethylene to ethanol employs non-renewable oil as raw material, whereas limited production capacity of ethanol by fermentation of biomass materials cannot meet large-scale demands in various fields [3]. The synthesis of ethanol by DME carbonylation to MAc and MAc hydrogenation is a potential way from synthesis gas (CO + H₂, syngas) which can be derived readily from natural gas, coal and biomass [5,6].

Porous materials are important in widespread processes such as catalysis, molecular separations, energy and health, in which

porous zeolites have made the largest contribution to society so far, and the field is still developing rapidly [7,8]. The synthesis of porous materials by templates have been well reviewed in literature [9]. Researches on DME carbonylation by heterogeneous catalysts have been gaining much attention and great progress have been made on the active sites [10–12], the stability of catalysts [13] and the positive enhancement of metal atoms [14–16] since Fujimoto first reported that HMOR was effective for the catalysis of DME to MAc in 1984 [17].

The intermediates and elementary steps of DME carbonylation reaction on zeolites have been proposed by Iglesia et al. [10,18,19]. They suggested that DME first adsorbed on the Brønsted acid sites of zeolite to form methanol and a chemisorbed methyl group CH₃* at zeolite exchange sites, and then CO inserted the C–O between the chemisorbed methyl group CH₃* and the oxygen atom of zeolite framework to produce CH₃CO*. This crucial intermediate CH₃CO* reacted with another DME molecule to form MAc and the surface methyl group was regenerated. Therefore, the direct observation of CH₃* and CH₃CO* under real reaction conditions would be prerequisite to confirm this mechanism proposal.

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Cheung et al. had tried to prove this mechanism by infrared spectroscopy. They observed the surface acetyl CH_3CO^* by dissociative adsorption of acetic anhydride on HMOR zeolite at 438 K [19]. So, the acetyl came from the reaction of material containing carbonyl group and the O-H of zeolite, not from the reaction of DME and CO under the real carbonylation reaction conditions. In addition as described in article, acetic anhydride could only react with Brønsted acid sites in twelve-member ring (12MR) main channels but not access those in side-pockets of mordenite, which were considered as the real active centers of DME carbonylation reaction [10,11]. Andrzej Malek reported the observation of acetyl group in order to explore the source of the first C-C species in MTO reaction [20]. The systematic study about the mechanism of DME carbonylation reaction, especially the observation and the variation of intermediates, methoxyl and acetyl, under real DME carbonylation reaction conditions, would help us to understand the reaction in depth.

In order to relate the reaction products and the adsorbed species, in situ information is essential. In this sense, in situ DRIFT spectroscopy can be regarded as an ideal technique. DRIFT spectroscopy is an increasingly popular technique in catalysis research since Körtüüm and Griffiths proved its fundamental principle theoretically in 1970s. This technique has been widely used to characterize the catalyst and surface species prior to and under reaction conditions and thus can provide vital information about reactions. Moreover, it permits in-situ observation of the reactor bed in powdered or granular form without any catalyst manipulation, not in wafer with the negative effect of the diffusion of reactants and products. Therefore, DRIFT spectroscopy is an invaluable method for studying powders, rough-surfaced solids and the reactions on powders, which is close to the actual state of the true reactions [21,22], and this method has been successfully used to study the mechanism of many reactions, such as the low-temperature methanol synthesis mechanism using ethanol promoter [23], the selective catalytic reduction of NO_x with NH_3 [24–26], the ethanol steam-reforming reaction [27], water-gas shift reaction [28] and CO oxidation at room temperature on Au/SiO_2 [29]. In this study, we used in situ DRIFT spectroscopy to study DME carbonylation reaction and observed the intermediates of methoxyl and acetyl groups on HMOR by DME reacting with CO under the real reaction conditions. Systematic study was carried out about DME adsorption on the HMOR, the effect of temperature and pressure on the acetyl formation and side reactions and the distinct effect of acid sites at different channels of HMOR on DME carbonylation reaction.

2. Experiment

2.1. Catalysts preparation

The materials, synthesis processes and characterization results of HMOR were presented elsewhere [15]. The sample marked as HMOR-MC (with acid sites only in 12MR main channels and the counter ions in 8MR side pockets were Na^+) was obtained by the ion exchange of NaMOR with NH_4NO_3 aqueous solution (0.1 mol L^{-1} , 1 g of the solid in 10 mL of the solution) at room temperature for 0.5 h. After filtered and washed with deionized water, the solid was dried and calcined in flowing dry air. Na content left in HMOR-MC was 2.5 wt% analyzed by XRF, about 53% of the total Na content in NaMOR 4.7 wt%. HMOR-SP (with acid sites in 8MR side pockets only) was prepared by adsorption of pyridine molecules to neutralize the acid sites in 12MR main channels of HMOR [13,30].

2.2. In situ DRIFT spectroscopy study

In situ DRIFT spectra were collected on a Bruke Tensor 27 instrument supplied with a diffuse reflectance attachment and with a

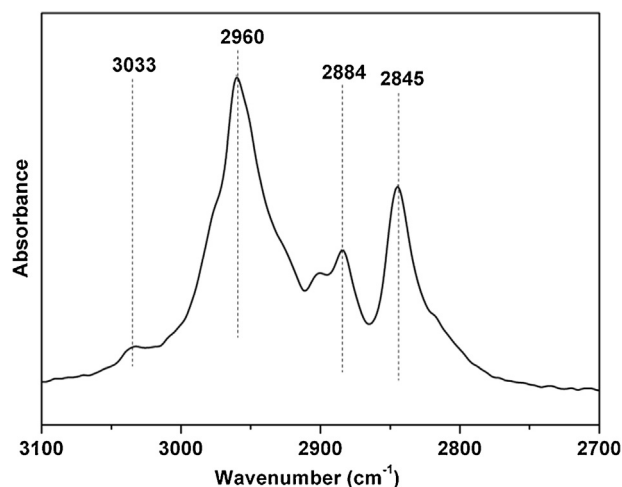


Fig. 1. In situ DRIFT spectrum of DME on $\gamma\text{-Al}_2\text{O}_3$ at 403 K.

MCT detector. The catalyst powder was contained in the diffuse reflectance infrared cell with ZnSe window which could work at high temperatures and high pressures. In situ absorbance spectra were obtained by collecting 16 scans at 4 cm^{-1} resolution.

DME used in experiments was 3% in volume and N_2 was the equilibrium gas. The degree of purity of CO and purging N_2 was 99.999%, respectively.

Before the adsorption of reactants, the sample was first calcined in situ in N_2 stream flowing $30 \text{ cm}^3 \text{ min}^{-1}$ at 723 K (523 K for HMOR-SP) for 120 min. Subsequently the catalyst was cooled down to adsorption temperature in N_2 stream, and the spectrum of catalyst was recorded as reference.

The spectra could be obtained continuously during the adsorption and reaction processes thus we could study the variation of surface intermediates over time. The spectra were obtained according to the following procedure after the catalyst pretreatment: the activated catalyst was exposed to DME at a total rate of $10 \text{ cm}^3 \text{ min}^{-1}$ at reaction temperature for 5 min, followed by sweeping in N_2 for 30 min to yield the adsorbed DME species on catalyst surface. As gaseous CO did not have effect on the observation and intensity of acetyl bands, so the spectra of acetyl were obtained continuously as CO passed through the in situ cell at different temperatures and pressures. Then DME was carried into the cell again. Gaseous products were observed by online mass spectrometer (Omnistar).

3. Results and discussion

3.1. Adsorption of DME on aluminum hydroxyls, silanols and Brønsted acid sites

In situ DRIFT spectra of DME adsorption on aluminum hydroxyl (AIOH), silanol (SiOH) and HMOR are shown in Figs. 1–4. The adsorptions of DME on AIOH and SiOH were conducted on $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 , mainly with the AIOH and SiOH at 3660 and 3740 cm^{-1} , respectively. There are four bands, 3033, 2960, 2884 and 2845 cm^{-1} , in the spectrum of DME adsorption on AIOH in Fig. 1. Assignment of the bands was made by analogy with the spectrum of known compounds and by comparison with published literatures. The bands at 3033 and 2960 cm^{-1} were the two asymmetric stretching modes of CH_3 , respectively. The band at 2845 cm^{-1} was the symmetric stretching mode of CH_3 . The 2884 cm^{-1} was assigned to the overtone of the deformation mode of CH_3 . Those bands indicated the formation of methoxyl groups of DME adsorption on AIOH at 403 K [31].

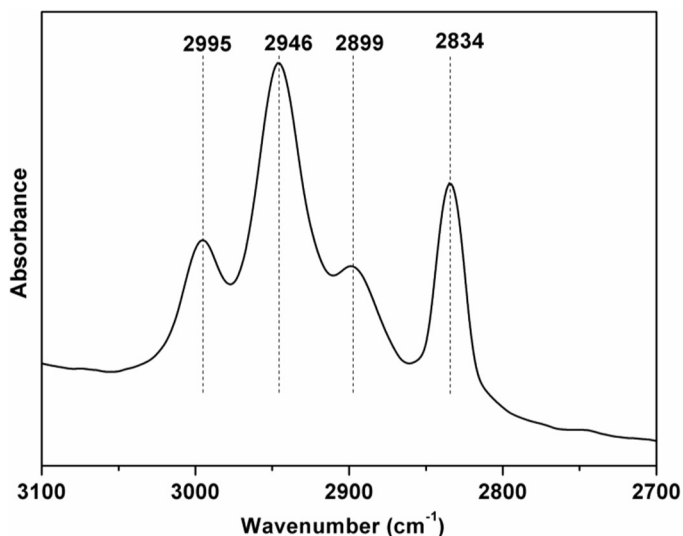


Fig. 2. In situ DRIFT spectrum of DME on SiO₂ at 403 K.

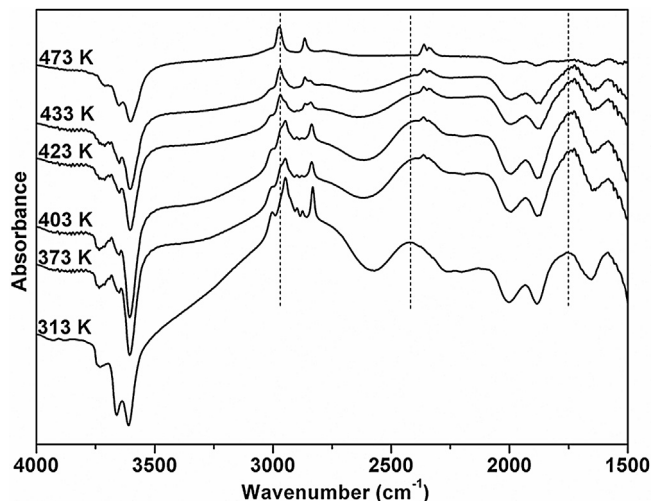


Fig. 3. In situ DRIFT spectra of DME on HMOR from 313 K to 473 K.

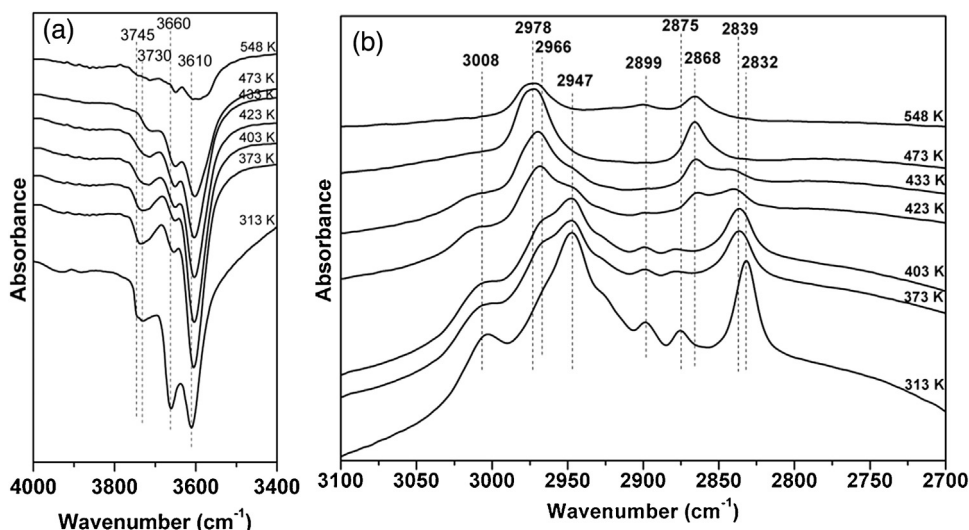


Fig. 4. In situ DRIFT spectra in O-H and C-H regions of DME adsorption on HMOR at different temperatures (a: O-H region, b: C-H region).

The spectrum of DME adsorption on SiOH of SiO₂ at 403 K is shown in Fig. 2. The four bands in the spectrum are at 2995, 2946, 2899 and 2834 cm⁻¹. DME adsorption on HZSM-5 (Si/Al = 121) with mainly SiOH at 423 and 473 K presented four bands at 2993, 2949, 2897 and 2836 cm⁻¹, assigned to the molecularly adsorbed DME, which interacted with silanol groups in zeolite through hydrogen bonding [32]. Therefore, the four bands in Fig. 2 were assigned to bands of molecularly adsorbed DME to the SiOH groups by hydrogen bonding.

Fig. 3 shows the DRIFT spectra of DME adsorption on HMOR at different temperatures. The saturated adsorption of DME on HMOR was conducted at 313 K first and then the equilibrium temperatures increased to certain point progressively and held for 20 min in N₂ stream. The spectra were obtained by deducting the zeolite skeleton as reference. A series of broad bands could be observed at around 3000, 2400 and 1700 cm⁻¹ below 433 K, losing intensity gradually with the increase of temperature. These three broad bands may come from the H-bonding complex and be attributed to the perturbed OH vibration, because they were quite similar to the A-B-C triplet bands of the hydroxyl groups reported previously [33,34]. Usually, for the H-bonding complex, the A-B-C pattern with broad and intense absorbance at around 2800, 2400, and 1700 cm⁻¹ was caused by a Fermi resonance between out-of-plane deformation vibration of bridged OH group and the perturbed hydrogen-bound OH group due to O-H...X-H formation. The appearance of A-B-C triplet indicated that the DME interacted with the Brønsted acid sites by hydrogen bonds as a neutral molecule [32]. The disappearance of A-B-C triplet with the temperature increase implied that the hydrogen bonded DME started to decompose.

In situ DRIFT spectra in O-H and C-H regions of DME adsorption on HMOR at different temperatures are presented in Fig. 4(a) and (b) in detail. The adsorption of DME induced the negative bands at 3745, 3730, 3660 and 3610 cm⁻¹ at 313 K. The presence of negative bands in O-H region signified that DME interacted with these kinds of hydroxyls. The band at 3610 cm⁻¹ was attributed to the Brønsted acid sites, combination of Brønsted acid sites in 12MR and 8MR channels of mordenite [10]. The band at 3660 cm⁻¹ was associated with the AlOH formed by the extra-framework Al species dropped from the tetrahedral sites in mordenite framework. The bands at 3730 and 3745 cm⁻¹ could be assigned to the internal and terminal or external SiOH groups. All the O-H peak positions of these bands shifted towards low wave number slightly with the increase of temperature. The intensity of negative O-H, especially those of Si-OH

Table 1
Vibration wave numbers of adsorbed species on HMOR.

Species	Frequency (cm ⁻¹)
DME hydrogen-bonded to SiOH	2995, 2946, 2899, 2834
DME hydrogen-bonded to SiOHAl	3008, 2966, 2947, 2839
AlOCH ₃	3033, 2960, 2884, 2845
SiOCH ₃ Al	2978, 2868
C=O in acetyl	1704
(C=C) _n	1600, 1490
Adsorbed water	1640

and Al-OH, decreased with the increase of temperature, inferring that DME desorbed from acid sites and the interaction between DME and Si-OH and Al-OH groups was weak.

We have attempted to assign the bands in C–H region in spectra of DME adsorption on HMOR above, which contained SiOH, AlOH and SiOHAl, at different temperatures in Fig. 4(b). Because of the relative intensity of bands and the overlapping one another, DME molecules on silica and methoxy species on alumina presented in Figs. 1 and 2 were part, but not all, observed in Fig. 4(b). According to the literature and DME adsorption on Brønsted acid sites, silanol and aluminum hydroxyl investigated above, the bands at 2947, 2899 and 2832 cm⁻¹ were assigned to the DME adsorption on SiOH groups by hydrogen bonds at 313 K. As the temperature increased to 403 K, the spectrum was different from that of 313 K. The bands at 3008 and 2947 cm⁻¹ lost intensity and a new shoulder band at 2966 cm⁻¹ appeared, the band at 2832 cm⁻¹ shifted to 2839 cm⁻¹, the band at 2899 cm⁻¹ almost disappeared, the bands at 3008, 2966 and 2839 cm⁻¹ were assigned to the DME interaction with the Brønsted acid sites by hydrogen bond. The bands of DME adsorption on AlOH would be underly by hydrogen bonded DME. The adsorbed DME started to decompose as the temperature above 423 K. Only two bands at 2978 and 2868 cm⁻¹ were observed at 473 K, which was the asymmetric and symmetric stretching modes of –CH₃ [19], indicating the formation of methoxyl groups by reaction of DME and Brønsted acid sites. The intensity of methoxyl bands decreased with the increase of temperature. Assignment of bands in Fig. 4(b) and in the following text is concluded in Table 1.

3.2. DME carbonylation by combination of in situ DRIFT spectroscopy and on line MS

DME carbonylation reaction was conducted in the in situ DRIFT cell, and gaseous fluent was monitored by on line mass spectrometer. The saturated adsorption of DME on HMOR was finished in several minutes at 473 K, accompanied by the observation of a burst of methanol and water by the mass spectrometry when the zeolite was first contacted with DME (not shown) and then DME in cell was flushed by N₂ at reaction temperature to remove the gaseous and physisorbed DME. Spectrum collected as N₂ flushed the cell is shown in Fig. 5(a). There are two bands, 2978 and 2868 cm⁻¹, left in the end which are ascribed to the stretching modes of –CH₃, signifying the formation of surface methoxyl groups.

Then, CO at 1.5 MPa was carried into the cell to react with methoxyls. As shown in Fig. 5(b), a new band at ~1704 cm⁻¹, which was ascribed to the $\nu(\text{C}=\text{O})$ stretch of the acetyl-zeolite intermediate [19,35], was observed after the introduction of CO, demonstrating the carbonylation reaction of CO with methoxyl occurred. Another proof was that the intensity of bands in C–H stretching region also changed along with the formation of acetyls as shown in Fig. 5(b), because it is well known that the intensity of CH₃ would decrease significantly when CH₃ groups are connected with electronegative groups C=O.

The intensity of infrared absorption depends on the magnitude of the transition probability and the change of the dipole moment of the vibration. To be more specific, the intensity of

infrared absorption is related to the concentration of functional groups and the chemical environment i.e. the attached chemical groups. Therefore caution is recommended when spectra are compared quantitatively. In this reaction, the intensity and shape of CH₃ were also influenced by other side reactions, such as the transformation of methoxyl with the products of the high-polymerized alkenes, (C=C)_n or coke species that were signed by the bands at ~1600 and 1490 cm⁻¹ [36]. The above mentioned phenomena were in good accordance with the result that the bands in C–H region also became broader than those of methoxyls due to the formation of a small amount of aliphatic hydrocarbon pool accompanied with the reaction of methoxyls into olefins [20]. More importantly, the acetyl was observed under the real carbonylation reaction conditions by the reaction of CO and methoxyl on HMOR. The intensity of acetyl band increased slowly in 1 h, after then it had little change, implying the end of the reaction of CO with methoxyl to acetyl. Then the gas phase carbon monoxide was flushed by N₂ from the cell. DME was introduced into the cell again to react with the acetyl. The band of C=O in acetyl changed almost instantaneously as DME contacted with acetyl. The change of acetyl with the time is presented in Fig. 5(c). The bands at 1776 and 1758 cm⁻¹ were ascribed to the C=O stretches in gaseous MAc [13,19], signifying that there was MAc product after the acetyl reacted with DME, which was also observed by the on line mass spectrometer (m/e = 74) in Fig. 6. The intensity of band (m/e = 74) increased also instantaneously when DME passed through the cell, and then started to diminish gradually after the peak value.

The C–H region in spectra after N₂ flush for 30 min is shown in Fig. 5(d), the methoxyl groups formed again.

The direct observation of acetyl under real reaction conditions by CO reaction with methoxyl demonstrated the intermediate effect of acetyl. It was noteworthy that the formation rate of acetyl, 1 h for the complete reaction, was slower than that of methoxyl, which formed on acid sites in several minutes and also slower than the following acetyl reaction with DME (shown in Fig. 5(c) and Fig. 6).

The observation of all of the intermediates also proved that the designed in situ DRIFT experimental process was practical and feasible for the study of DME carbonylation.

3.3. Effect of reaction pressure on the formation of acetyl

A detailed DRIFT spectroscopy study was performed to gain a better understanding of the effect of pressure on the formation of acetyl. CO was carried into in situ cell under different pressures after DME was absorbed on activated HMOR at 473 K. The spectra of adsorbed species on catalysts under 0, 0.5, 1.5 and 3.0 MPa for 10, 30 and 60 min were recorded and are shown in Fig. 7. The Beer-Lambert Law is the base for the quantitative spectrometric analysis. There are many chemical and instrument factors to influence the intensity of infrared absorption so only semi-quantitative analysis is possible from the infrared spectrum. As for the DRIFT spectroscopy, the catalyst sample was placed in the crucible, and the gaseous reactant reacted with the acid sites on the surface of catalyst to produce the adsorbed species. Therefore, it is more difficult for the quantitative analysis by DRIFT spectrum. However, the intensity of band in DRIFT spectrum for the functional groups in the identical chemical environment from one sample is proportional to the concentration of the studied functional group. Therefore it is possible to study the variation trend of functional group over time by the in situ DRIFT spectroscopy in such circumstances. From Fig. 7(a), the C=O in acetyl (CH₃CO) at ~1704 cm⁻¹ was not observed when the carbonylation reaction was conducted at atmosphere pressure for 10 min, meaning that acetyl was not formed by the reaction CO and methoxyl. However, the band at ~1600 cm⁻¹, attributed to the high polymerized alkenes (C=C)_n or

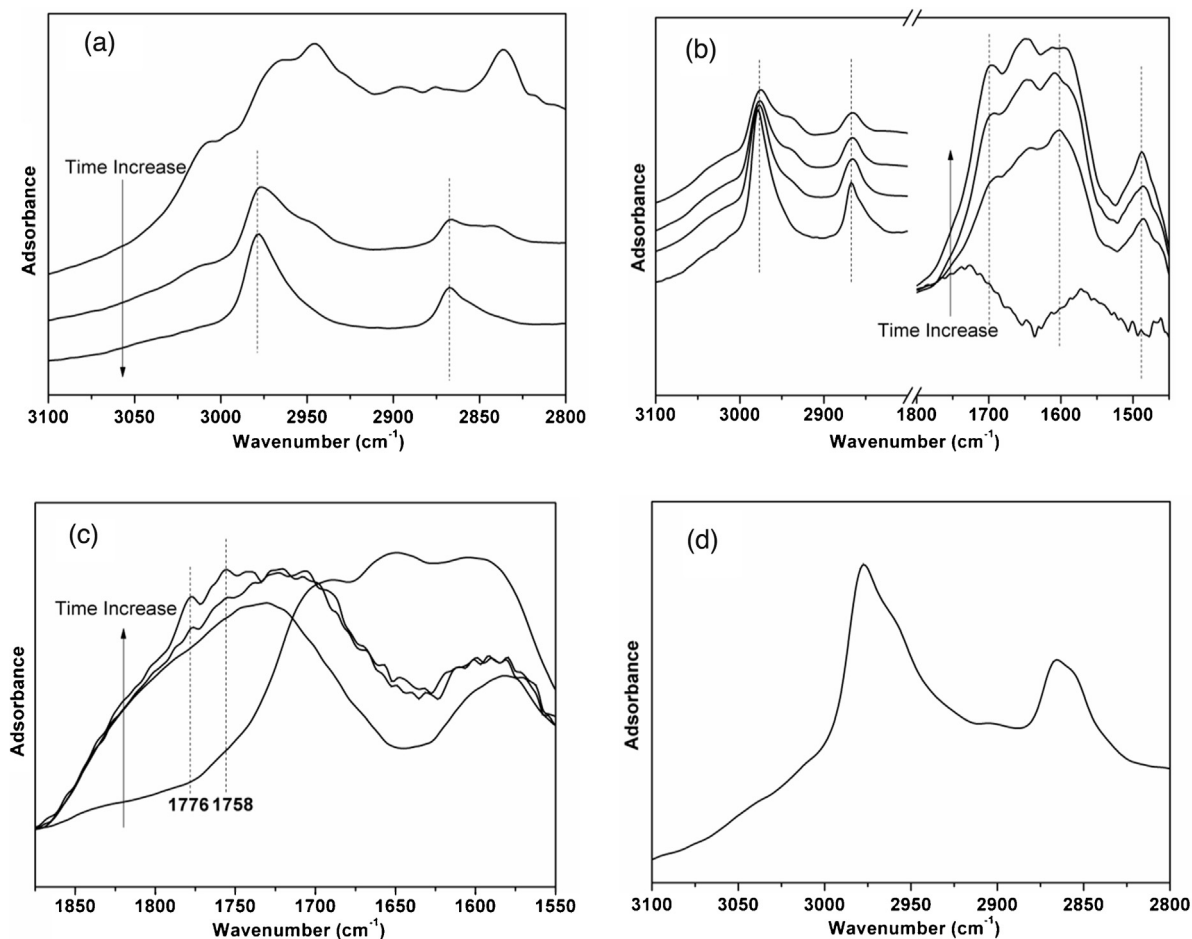


Fig. 5. In situ DRIFT spectra of DME carbonylation conducted in the in situ cell (a: DME adsorption on HMOR at 473 K, b: Acetyl formation at 473 K and 1.5 MPa for 1 h, c: MAc formation at 473 K, d: Infrared spectrum in C-H region after carbonylation reaction at 473 K).

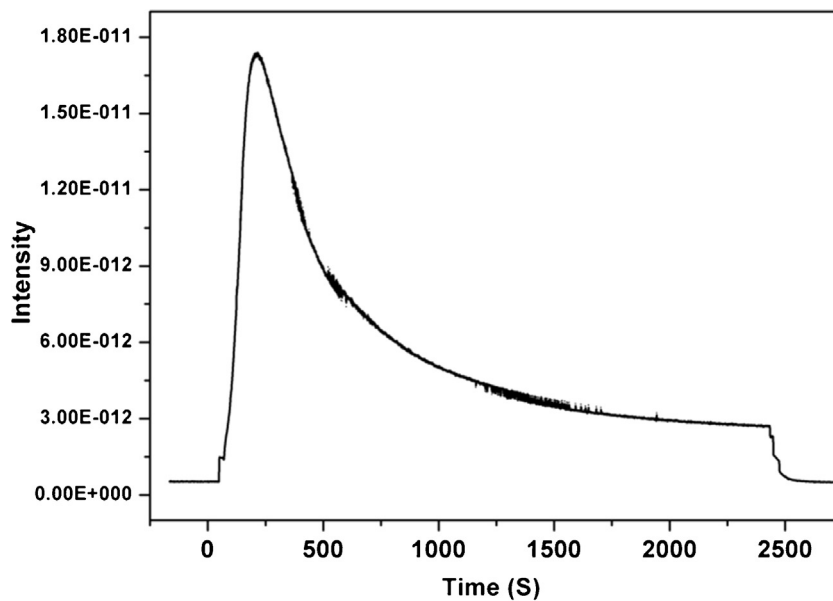


Fig. 6. The intensity of m/e at 74 in MS after DME introduced into the cell.

coke species, was obvious, indicating that methoxyl on the surface of HMOR transformed into olefin and then into cokes through polymerization and hydrogen transfer reactions [36]. Therefore, the reaction into olefin was favored in comparison with the DME

carbonylation reaction under atmospheric pressure. The band of C=O in acetyl at $\sim 1704 \text{ cm}^{-1}$ was observed as the pressure up to 0.5 MPa at 10 min. The intensity of the bands at $\sim 1704 \text{ cm}^{-1}$ continued to increase with the pressure up to 1.5 MPa and 3.0 MPa at

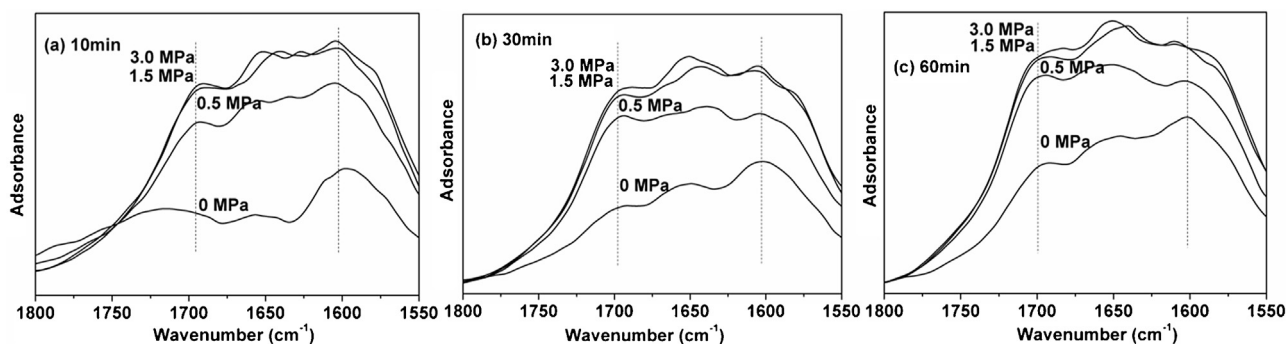


Fig. 7. In situ DRIFT spectra of acetyl at 473 K under different pressures ((a): 10 min, (b): 30 min, (c): 60 min).

10 min, therefore high pressure could promote the insertion reaction. The C=O in acetyl at $\sim 1704\text{ cm}^{-1}$ in spectrum was observed under atmosphere pressure after CO was carried into the cell in situ for 30 min, indicating that the carbonylation reaction could occur under atmosphere pressure though the side reactions into cokes were favored. The intensity of the acetyl for the 0.5, 1.5 and 3.0 MPa became stronger as the time was prolonged from 10 to 30 min. Moreover, the increase rate of band at $\sim 1704\text{ cm}^{-1}$ was quicker than that of $\sim 1600\text{ cm}^{-1}$. The intensity of all of the bands continued to increase at the reaction time for 60 min. It was noticeable that the effect of pressure on the formation of acetyl declined with the extended reaction time by comparing the intensity of acetyl in Fig. 7(c) and (a). Andrzej Malek compared the acetyl under high and low CO pressure and found that only under high CO pressure could the acetyl group accumulate to substantial amount for spectroscopic observation; on the contrary, other competing reactions would either consume the active Brønsted methyl groups or react with the acetyl groups at low CO pressure. Therefore, the acetyl could not be observed by the IR [20]. However, it was clear in our study that the spectrum of acetyl could be observed at atmosphere pressure even though it would take longer time to accumulate for observation.

Therefore, the carbonylation and cokes formation reactions were competitive under high pressure, and methoxyl tended to transform into cokes under atmosphere pressure in comparison with the carbonylation. DME carbonylation reaction should be conducted under high pressure.

3.4. Effect of reaction temperature on DME carbonylation

The carbonylation reactions by in situ DRIFT spectroscopy were conducted at different temperatures in order to investigate the effect of temperature on the formation of intermediates and side reactions. After DME adsorbed on the catalysts with saturation loading at different reaction temperatures, nitrogen was introduced into the in situ cell for 30 min to degas the gaseous DME. The DRIFT spectra in C-H region after the adsorption of DME are shown in Fig. 8. The result was repeatable in comparison with that of Fig. 4, indicating the reliability of designed experiment process. The bands at 2978 and 2868 cm^{-1} , attributing to the asymmetric and symmetric stretching vibrations of methyl group, were not present at 403 K, and could be observed at 433 K though there were also other bands with different adsorbed forms of DME on acid sites. The methoxyl groups were formed completely above 473 K. The bands gradually lost intensity with the increase of temperature, methoxyl desorbed or transformed into other species.

The DRIFT spectra of C=O in acetyl after carbon monoxide reacted with DME adsorbed on surface for 60 min at different temperatures and 1.5 MPa is shown in Fig. 9. Reaction performed at 403 K for 60 min produced no significant change in spectrum,

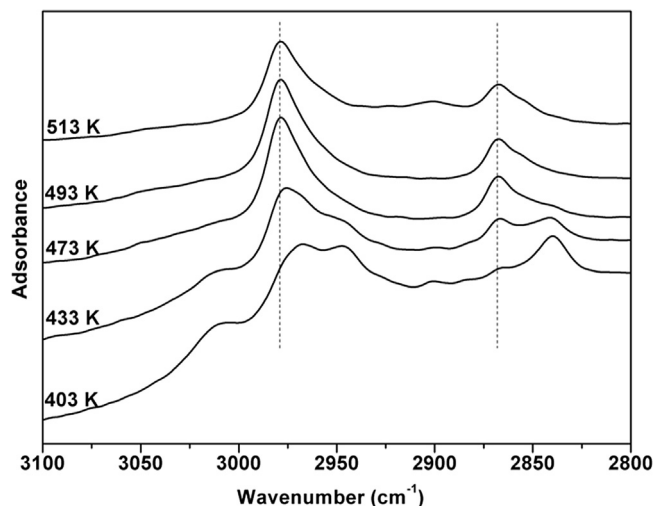


Fig. 8. In situ DRIFT spectra of DME adsorption on HMOR at different temperatures.

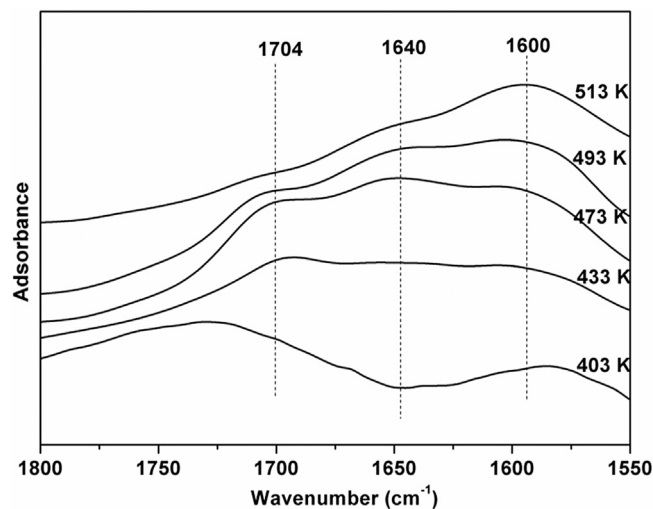


Fig. 9. In situ DRIFT spectra of acetyl on HMOR at different temperatures and 1.5 MPa.

meaning that no conversion occurred at 403 K. There was no methoxyl and acetyl observed at 403 K, maybe inferring that the formation of methoxyl was necessary for the insertion reaction of CO. The C=O in acetyl at $\sim 1704\text{ cm}^{-1}$ was observed as CO contacted with adsorbed species on the surface of HMOR at 433 K and 1.5 MPa in Fig. 9, suggesting that insertion of CO into methoxyl occurred. The interesting and relevant changes appeared starting at 433 K, so the conversion may start from this temperature. The conversion

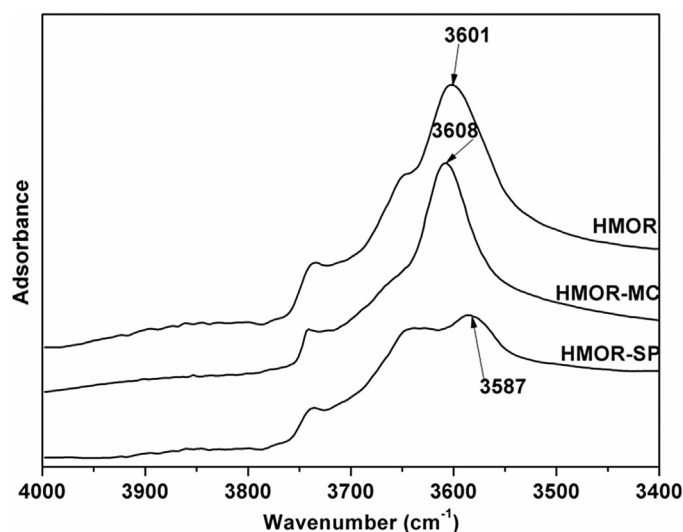


Fig. 10. In situ DRIFT spectra in O-H region of HMOR, HMOR-SP and HMOR-MC at 473 K.

was enhanced comparing with that at lower reaction temperature as the vibration band of (C=O) (1704 cm^{-1}) at 473 K became more remarkable. The band intensity of (C=O) gradually decreased with the increasing of temperature to 493 and 513 K, maybe because methoxyls and acetyls on the surface of zeolite transformed into other species at high temperatures.

Three main bands are observed in the region of $1800\text{--}1550\text{ cm}^{-1}$ in Fig. 9, the band at $\sim 1704\text{ cm}^{-1}$ assigned to C=O in acetyl, the band at $\sim 1600\text{ cm}^{-1}$ attributed to the high polymerized alkenes (C=C)_n, or coke species [36], the band at around 1640 cm^{-1} belonged to water accompanied with the formation of hydrocarbons at $\sim 1600\text{ cm}^{-1}$. The appearance of band at $\sim 1600\text{ cm}^{-1}$ demonstrated the occurrence of alkene polymerization or coke formation when the conversion was carried out at relatively high temperature. On a further temperature increase to 513 K, the band at $\sim 1600\text{ cm}^{-1}$ became more prominent with enhanced hydrogen transfer and polymerization reactions. It could be obtained that more coke was formed on the surface of HMOR as the temperature increased. In conclusion, high temperature was in favor of the formation of hydrocarbons in comparison with DME carbonylation.

3.5. Study of DME carbonylation on acid sites at different channels of HMOR

Bhan and his co-workers [10] reported that the insertion of CO into chemisorbed methyl groups occurred selectively within 8MR zeolite channels. Boronat et al. [11] further pointed out that it was the T3-O33 position effective for the insertion reaction because of the unusual orientation of the methoxy group with respect to the 8MR channel (parallel to the cylinder axis) by quantum-chemical methods. Here, we studied the respective effect of acid sites in 8MR and 12MR channels of mordenite on DME carbonylation by in situ DRIFT spectroscopy.

The spectra in O–H region of catalysts treated in N₂ stream within the in situ cell then cooled to 473 K and pyridine adsorbed in HMOR-SP are shown in Fig. 10 and Fig. S1. The bands of O–H were at ~ 3601 , 3608 and 3587 cm^{-1} for HMOR, HMOR-MC, HMOR-SP, respectively. The antisymmetric O–H stretch spectrum in H-MOR can be deconvoluted into two types of O-H species, with bands at $\sim 3610\text{ cm}^{-1}$ for H⁺ in 12MR main channels and at $\sim 3590\text{ cm}^{-1}$ for H⁺ sites in 8MR side pockets [10,37,38]. Therefore, the acid sites in HMOR-MC and HMOR-SP had been distinguished from each other, meaning the HMOR-MC with the acid sites only in 12MR

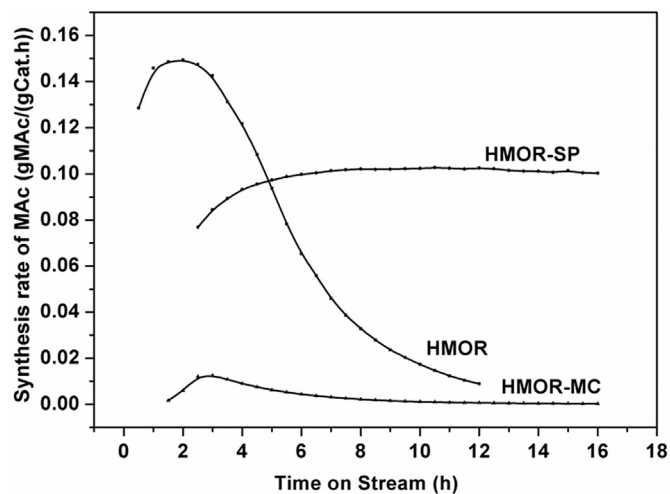


Fig. 11. The synthesis rate of MAC (gMAC/(gCat.h)) over HMOR, HMOR-SP and HMOR-MC catalysts. Reaction conditions: 473 K, 2.0 MPa, 5%DME, 35%CO, and 60%H₂, 1500 mL/(gCat.h).

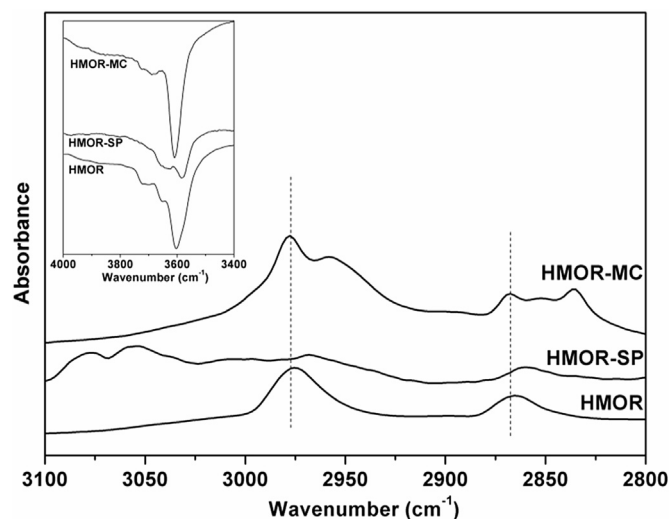


Fig. 12. In situ DRIFT spectra of DME adsorption on HMOR, HMOR-MC and HMOR-SP at 473 K.

main channels and HMOR-SP with acid sites only in side pockets. The quantitative calculation of the amounts of acid sites in HMOR, HMOR-SP, HMOR-MC was conducted according to the results of ¹H MAS NMR spectra (Fig. S2), 47% in 12MR main channels and 53% in 8MR side pockets of mordenite. The distribution of acid sites was similar with the results in literatures [12,13], and was the base to study DME carbonylation reaction with specific active sites.

Change in synthesis rate of MAC (gMAC/(gCat.h)) with time-on-stream (TOS) for HMOR, HMOR-SP, HMOR-MC catalysts is shown in Fig. 11. For HMOR, synthesis rate increased quickly after a short induction period and then declined soon, indicating that the catalyst started to deactivate. But for HMOR-SP with acid sites in 8MR side pockets, the induction period prolonged and more obviously, the synthesis rate was stable for 16 h on stream without deactivation. The synthesis rate for HMOR-MC was extremely low in comparison with that of HMOR and HMOR-SP. The difference of synthesis rate among HMOR, HMOR-SP and HMOR-MC catalysts probably indicated the distinct effect of acid sites in different channels of mordenite on DME carbonylation reaction.

The DRIFT spectra in C–H region after adsorption of DME on three samples at 473 K are presented in Fig. 12, and the inset shows

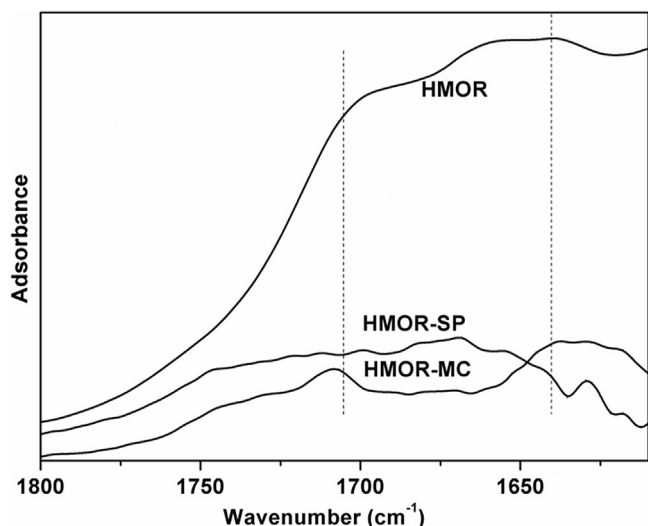


Fig. 13. In situ DRIFT spectra of C=O in acetyl for HMOR, HMOR-MC and HMOR-SP.

the corresponding O–H spectra. The methoxyl was formed completely on HMOR, and the negative O–H was at around 3603 cm^{-1} at 473 K. However, the intensity of methoxyl on HMOR-SP was relatively weak in comparison with that on HMOR, even the adsorption was completed at high pressure for long time, far less than 53% of the intensity of methoxyl on HMOR, which was the concentration of H^+ in 8MR side-pockets characterized by the ^1H MAS NMR technique. The acid sites in 12MR main channels of HMOR-SP were deactivated by the basic pyridine molecules. It was reasonable that the pore volume and channels of 12MR main channels were blocked to certain extent. The 8MR side pockets were connected with 12MR main channels and the reactants and products diffused into and out zeolite through 12MR main channels. Therefore the pyridine molecules adsorbed in 12MR main channels blocked the diffusion of DME into 8MR side pocket and resulted in the lower utilization rate of acid sites in side pockets of mordenite. The C–H region spectrum after DME saturated adsorption on HMOR-MC is also shown in Fig. 12. The bands at 2978 and 2868 cm^{-1} ascribed to CH_3 were very strong, thus there were methoxyls formed on HMOR-MC.

The bands of C=O in acetyl groups, formed by the reaction of CO with methoxyl on HMOR, HMOR-SP and HMOR-MC are shown in Fig. 13. The acetyl on HMOR was intense but that on HMOR-SP was weak maybe because of the weak intensity of methoxyl on HMOR-

SP shown in Fig. 12. The band at around 1640 cm^{-1} assigned to the adsorbed water was not observed on HMOR-SP, illustrating that there was no water and coke formed as the carbonylation reaction proceeded in 8MR side pockets of mordenite, which was consistent with the better stability of HMOR-SP shown in Fig. 11. However, the acetyl formed on HMOR-MC was very weak in comparison with that of HMOR, although the intense methoxyl species was observed on HMOR-MC in Fig. 12, illustrating that the insertion reaction of CO into the methoxyl was almost unavailable owing to the lack of space confinement. On the contrary, the band at 1640 cm^{-1} along with the formation of water was strong in comparison with that on HMOR-SP. Therefore, the acetyl could form on the acid sites in 12MR main channels of mordenite but the yield was very low. Li et al. [12] observed the acetaldehyde, not the acetyl groups, considered as the intermediate to MAC in 12MR main channels of mordenite by in-situ solid state NMR spectroscopy.

The in situ DRIFT spectroscopy results were illustrative of DME catalytic test consequences in Fig. 11. The stability of HMOR-SP was improved greatly with relative low synthesis rate of MAC in comparison with that on HMOR because of the blocked diffusion of reactants and products by adsorbed pyridine molecules in 12MR main channels. The synthesis rate was lowest on the acid sites in 12MR main channels accompanied with the formation of coke.

4. Conclusions

Base on the observation above by in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, a possible mechanism for the DME carbonylation and side reactions is offered as a scheme of Fig. 14. The methoxyl, chemisorbed DME on the acid sites, was observed above 433 K. Reaction of methoxyl and CO generated acetyl and then acetyl reacted with DME to produce MAC and to regenerate methoxyl again. The formation of acetyl took longer time than those of the saturation adsorption of DME and the reaction of acetyl with DME, implying that the insertion of CO into methoxyl was the rate-controlling step in DME carbonylation. The reaction of DME into olefins was favored at low pressure and high temperature, whereas high pressure promoted the DME carbonylation reaction. The in situ carbonylation reactions in different channels of mordenite demonstrated that the acid sites both in side pockets and 12MR main channels of mordenite were active for the formation of acetyl. Meanwhile, acid sites in side pockets were more active for carbonylation than those in 12MR main channels which favored the formation of coke.

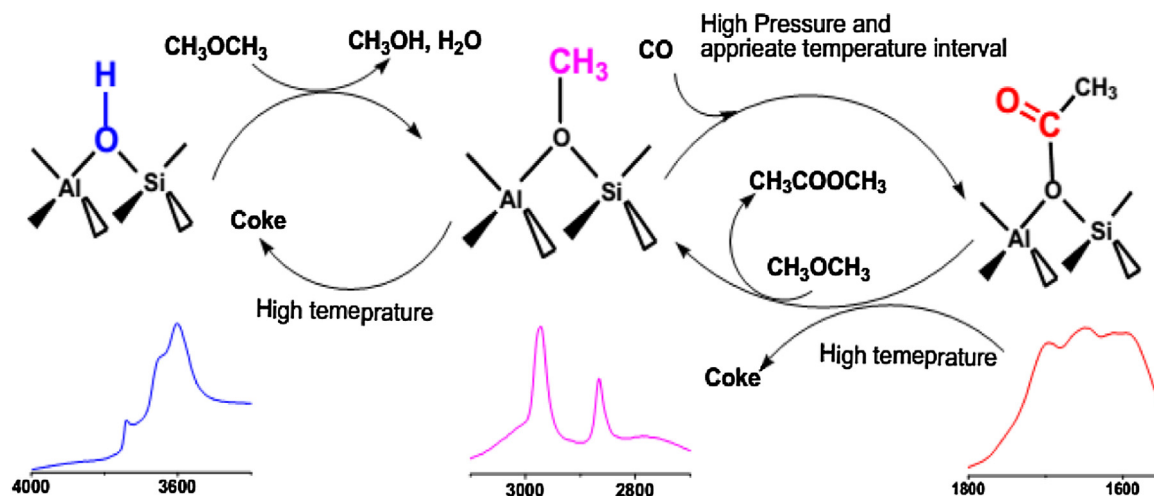


Fig. 14. Proposed mechanism for the DME carbonylation and side reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2016.02.032>.

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