Journal of Catalysis 335 (2016) 47–57

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Methanol to hydrocarbons reaction over Hβ zeolites studied by high resolution solid-state NMR spectroscopy: Carbenium ions formation and reaction mechanism

Mozhi Zhang [a,e,1], Shutao Xu [a,1], Jinzhe Li [a], Yingxu Wei [a,*], Yanjun Gong [b], Yueying Chu [c], Anmin Zheng [c], Jinbang Wang [a,e], Wenna Zhang [a,e], Xinqiang Wu [a,e], Feng Deng [c], Zhongmin Liu [a,d,*]

[a] National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China
[b] State Key Laboratory of Heavy Oil Processing, CNPC Key Laboratory of Catalysis, China University of Petroleum-Beijing, Beijing 102249, PR China
[c] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, National Center for Magnetic Resonance in Wuhan, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, PR China
[d] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China
[e] University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 2 April 2015
Revised 24 November 2015
Accepted 14 December 2015

Dedicated to Professor Jean-Pierre Gilson on the occasion of his 60th birthday when accepted.

Keywords:
Methanol-to-hydrocarbons
^{13}C MAS NMR
Carbenium ions
Methylcyclopentenyl cations
Heptamethylbenzenium cation

ABSTRACT

Carbenium ions as active intermediates play very important roles in methanol conversion to hydrocarbons (MTH) reactions, while their observation and structure confirmation is of great difficulty. In this contribution, solid-state magic-angle-spinning (MAS) NMR spectroscopy has been applied in the investigation of methanol conversions over Hβ zeolite. By attempting the batch-like and continuous-flow reactions over the catalysts with varied acid site densities and under the condition of different reaction temperatures and atmosphere pressures, an optimized way for direct observation of carbenium ions has been developed. For the first time, two types of carbenium ions, including methylcyclopentenyl (MCP^+) cations and heptamethylbenzenium (heptaMB$^+$) cation, have been successfully captured by ^{13}C MAS NMR during methanol conversion over Hβ zeolite. For the batch-like reactions, methanol conversion and carbenium ions observation have been promoted by using the Hβ catalysts with more Brönsted acid sites and performing the reaction under relatively high atmosphere pressure. The competitive adsorption from reactants and products on the catalyst surface may cause the deprotonation of the carbenium ions. In the continuous-flow reactions, both the heptaMB$^+$ and MCP^+ cations are formed and more easily observed compared with batch-like reactions due to the improved methanol conversion and the reduced competitive adsorption on the Brönsted acid sites. Based on the carbenium ions identification, a catalytic cycle is proposed to explain the generation of isobutene, a predominantly generated product on Hβ zeolite, during methanol conversion.

1. Introduction

Since 1970s, methanol conversions to hydrocarbons (MTH) processes have been developed for the production of olefins, gasoline and aromatics through non-petrochemical routes from abundant resources of coal or natural gas [1,2]. Light olefins, especially ethene and propene, serving as basic petrochemicals, play important roles in modern industry. Production of light olefins from methanol conversion (methanol-to-olefins, MTO), has received much attention from both academia and industry [3,4]. After 30 years R&D, MTO process industrialization has been achieved in China with the application of DMTO technology developed by Dalian Institute of Chemical Physics (DICP) [5,6]. Although the commercial MTH process, especially MTO process, has achieved a great success, the mechanism of methanol conversion has still not been thoroughly understood. The reaction mode of first C–C bond formation and the detailed catalytic routes of hydrocarbon generation remain elusive.

---

* Corresponding authors at: National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China (Y. Wei and Z. Liu). Fax: +86 411 84691570.
E-mail addresses: weiyx@dicp.ac.cn (Y. Wei), liuzm@dicp.ac.cn (Z. Liu).

[1] Both authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jcat.2015.12.007
0021-9517/© 2015 Elsevier Inc. All rights reserved.

In early 1980s, the researchers realized the autocatalysis of MTH reaction catalyzed by zeolites [7,8]. Even though some direct mechanism for C–C bond formation has been proposed [8–12], a more rational and energetically favorable reaction mechanism, hydrocarbon pool mechanism [13–17], has been proposed as an indirect mechanism and accepted more widely than other suggestions. The formation and identification of hydrocarbon pool species over the zeolite catalysts and their function in methanol conversion, as the key issues of mechanism investigation, have attracted wide research interests and intensive studies. For some catalysts with spacious channel or cavity structure, such as Hβ, HZSM-5, HSAPO-34, cyclic organics, i.e. methylbenzenium cations, methylcyclopentenyl cations and the deprotonated hydrocarbons have been proved to behave as the reaction intermediates during methanol conversion [18–21]. Some carbenium ions in MTO reaction have been discovered (Scheme 1) by magic-angle-spinning (MAS) NMR under different reaction conditions. Based on the determination of formed carbenium ions over specific zeolites or SAPO catalysts, the detailed reaction routes, side-chain methylation mechanism or paring mechanism, were proposed for the olefin product generation from methanol conversion [22–25].

The capture and structure determination of the active intermediates, especially carbenium ions, in MTO reaction is of great significance and difficulty. Carbenium ions are generally highly reactive due to their electron deficiency. Olah and coworkers developed super acid to stabilize the carbenium ions and made important contributions for the carbenium ion chemistry, including their structures and properties [26–29]. In general, the observation of carbenium ions depends on the acidity of the catalyst and the proton affinity (PA) of the neutral hydrocarbons [30]. Catalysts used in the MTH process are typically microporous solid acids, including zeolites and zeotype molecular sieves. Haw and coworkers reported that the acid strength of zeolites appeared to be no stronger than 80% H_2SO_4, and simple carbenium ions such as isopropyl cation were not observed in a zeolite [31]. They also predicted with the assistance of theoretical calculations that the carbenium ions can be persistent inside zeolites if the neutral hydrocarbons have a proton affinity value higher than 209 kcal/mol [30]. Recently, we found that the reactivity of carbenium ions in the chemical environment of the catalyst for methanol conversion should also be considered in the carbenium capture and observation in addition to the proton affinity value [32]. It is illustrated that the capture of the carbenium ions in MTO reaction strongly depends on the catalyst used and the reaction condition. For the zeolite catalysts with spacious cages or channels and strong acidities, bulky carbenium ions can be easily generated and stabilized for observation [18,20,33–34]. Conducting methanol conversion under optimized reaction conditions and developing sensitive measure methods will guarantee the formed carbenium ions to be captured and structure-determined before their further transformations, which makes it possible to establish the rational reaction mechanism with the involvement of these important intermediates.

In the present study, solid-state NMR investigation of methanol conversion is carried out under batch-like and continuous-flow reaction conditions using a series of Hβ zeolites with varied acid concentrations as catalysts. The conversions of methanol on the catalyst surface under different atmosphere pressures and reaction temperatures have been systemically studied and the important carbenium ions observation is realized under an optimized reaction condition with a post-treating method. Based on the identification of important carbenium ions with combined techniques of NMR, GC–MS and theoretically calculation, a catalytic cycle is proposed to explain the formation of a predominantly generated product, isobutene, on Hβ zeolite during methanol conversion.

2. Experimental

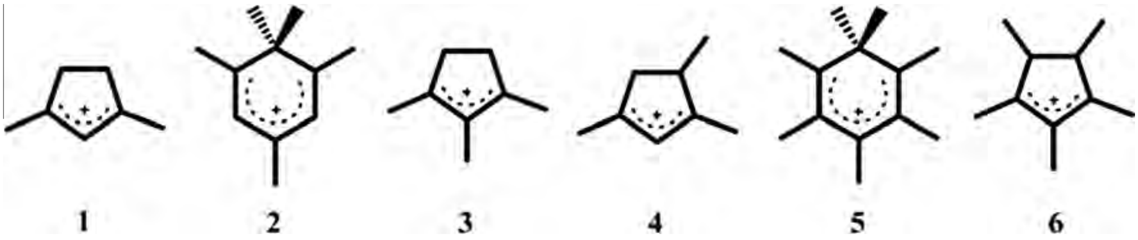
2.1. Catalysts

Four as-synthesized Naβ zeolites with different Si/Al ratios of 50, 38, 24 and 12 according to X-ray fluorescence (XRF) measurements were obtained from China University of Petroleum, Beijing. These Naβ zeolites were calcined in air at 550 °C for 6 h to remove the templates. The Hβ zeolites were obtained by transferring the calcined samples into NH_4^+ forms with three times ion-exchange in 1.0 M NH_4NO_3 aqueous solution at 80 °C and subsequently calcining the NH_4^+ form samples at 550 °C for 4 h. The obtained Hβ samples with Si/Al ratios of 48, 36, 24 and 13 are named as Hβ-1, -2, -3 and -4.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert PRO X-ray diffractometer with Cu-Kα (λ = 1.5418 Å), recording at 40 kV and 40 mA. The chemical compositions of as-synthesized and H-type zeolites were analyzed on a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal size and morphology were observed on a scanning electron microscope (SEM, Hitachi S-3400N). N_2 adsorption and desorption experiments were performed at 77 K on a Micromeritics ASAP 2020 physical adsorption analyzer [35].

All the solid-state NMR experiments were performed on a Bruker Avance III 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm or 7 mm MAS probe. The resonance frequencies were 150.9, 156.4, 119.2 and 600.13 MHz for ^{13}C, ^{27}Al, ^{29}Si and ^{1}H, respectively. ^{13}C MAS NMR spectra were recorded using high-power proton decoupling with a spinning rate of 12 kHz. 2048 scans were accumulated with a $\pi/4$ pulse width of 1.8 μs and a 4 s recycle delay. ^{13}C CP/MAS NMR spectra were recorded with a contact time of 3 ms and a recycle delay of 2 s. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. ^{27}Al MAS NMR experiments were performed with a spinning rate of 12 kHz using one pulse sequence. 600 scans were accumulated with a $\pi/8$ pulse width of 0.75 μs and a 2 s recycle delay. Chemical shifts were referenced to $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ at



Scheme 1. The series of carbenium ions formed in zeolites detected with NMR spectroscopy.

−0.4 ppm. ^{29}Si MAS NMR spectra were recorded with a spinning rate of 6 kHz using high-power proton decoupling. 1024 scans were accumulated with a $\pi/4$ pulse width of 2.5 μs and a 10 s recycle delay. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS) at 0 ppm. Before ^1H MAS NMR experiment, the samples were dehydrated typically at 693 K and a pressure below 10^{-3} Pa for 20 h. ^1H MAS NMR spectra were recorded using a single pulse sequence with a $\pi/4$ pulse of 2 μs and a 10 s recycle delay, with adamantane (1.74 ppm) as the chemical shift reference. For Brönsted acid density quantification, all samples were weighed and their ^1H MAS NMR spectra were resolved by Dmfit software with Gaussian–Lorentz line shapes, using hexamethylbenzene (1.6 ppm) as the quantitative external standard, measured under the same NMR acquisition condition [36,37]. $^1H/^{27}Al$ TRAPDOR (Transfer of Populations in Double Resonance) MAS NMR experiments [38] were operated in ^1H channel with a spin–echo sequence, at the same time during the first τ period using ^{27}Al irritation in another channel, with a spinning rate of 10 kHz and 32 accumulated scans.

2.3. ^{13}C MAS NMR study of methanol conversion and carbenium ions formation

In this contribution, two types of reactions of methanol conversion, batch-like (BA) reaction and continuous-flow (CF) reaction, were performed and studied by ^{13}C MAS NMR.

In the batch-like (BA) reactions, methanol conversion was performed in a sealed quartz tube as a batch reactor. Before reaction, the calcined Hβ zeolites were loaded in the reactor and dehydrated under vacuum (10^{-3} Pa) at 400 °C for 10 h. Upon the adsorption of $^{13}CH_3OH$ over the Hβ zeolites at room temperature for 20 min, the reactor was sealed and heated from room temperature to the reaction temperature 250 °C, 275 °C, 300 °C and 325 °C. The reaction was performed for 20 min under the reactant atmosphere with varied methanol pressures (5–80 kPa). For reaction with gas phase pressure of zero, after $^{13}CH_3OH$ adsorption at room temperature, the reactor was heated to 150 °C and kept at this temperature for 1 h to generate surface methoxyl groups, and then the reactor was evacuated at 160 °C for 2 h to remove the excess methanol vapor, followed by the reaction at 275 °C [39]. After all these reactions, the reactors were quenched immediately in liquid nitrogen and the catalysts were transferred to the NMR rotors in a glove box filled with inert nitrogen gas and then measured with ^{13}C MAS NMR.

In the continuous-flow (CF) reactions, methanol conversion was performed in a microscale fixed-bed reactor. Before reaction, the catalyst (100 mg, 40–60 mesh) was loaded in the reactor and activated at 500 °C in a He flow of 25 ml/min for 40 min and then the temperature of the reactor was adjusted to reaction temperature of 275 °C. The $^{13}CH_3OH$ was fed by passing the carrier gas (25 ml/min) through a saturator containing methanol at 14 °C, which gave a weight hourly space velocity (WHSV) of 2 h^{-1}. After the reaction, the catalysts were quickly cooled to stop the conversion and transferred in a glove box into 4 mm MAS NMR rotors for ^{13}C MAS NMR measurements. The effluent products from reactor were kept warm and analyzed online by a gas chromatography (GC) equipped with two FID detectors and a mass spectrometry detector (Agilent 7890B/5977A) using column switching and backflushing technique. The C_1–C_7 hydrocarbons and hydrocarbons higher than C_7 (C_7^+) were separated by DB-1. Detailed analysis of C_1–C_7 and C_7^+ was realized with capillary columns of PLOT-Q and HP-5 respectively.

2.4. Determination of retained compounds with GC–MS

After the reaction, part of the discharged catalysts was transferred to Teflon vials and dissolved in 20% (wt) HF solution for 1 h. After the complete dissolution, CH_2Cl_2, or CCl_4, was added into the Teflon vials to extract the liberated organic compounds confined in the catalysts. Before transferring to the separator, 5% (wt) NaOH solution was used to neutralize acidic solution. The CH_2Cl_2 (CCl_4)-extracted organic phase was analyzed by a gas chromatography (GC) equipped with a HP-5 capillary column, a FID detector and a mass spectrometric detector (Agilent 7890A/5975C) [40]. Hexachloroethane was used as the internal standard for the extracts.

2.5. Theoretical calculation

The geometry optimizations were performed by using the DMol3 program with the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) method. And the ultra soft pseudo potential, medium plane wave cutoff energy and a default medium level Monkhorst–Pack K-point in the DMol3 program were adopted to sample the Brillouin zone. In order to accurately describe the interactions between the carbenium ions and Hβ zeolite framework, the structure optimization and the following NMR calculation were done with DFT-D method, which includes adding a semi-empirical dispersion potential to the conventional Kohn–Sham DFT energy [41]. ^{13}C NMR shielding calculations were performed by the gauge including projection augmented wave (GIPAW) method in the MS CASTEP-NMR code at the GGA/PBE level based on the carbenium ions adsorbed structures inside the Hβ zeolite [42]. A fine K-point ($2 \times 2 \times 2$) and a cutoff energy of 550 eV were employed, combined with core–valance interactions described by an ultra soft pseudo potential generated on-the-fly. The ^{13}C calculated chemical shifts were further converted to $(\delta^{13}C)_{cal}$ values, which were referred to the absolute shielding of benzene.

3. Results and discussion

3.1. Varied framework Si/Al ratios and Brönsted acid site concentrations of Hβ zeolites

Powder XRD patterns (Fig. S1) confirm the four H-type samples possessing pure and well crystalline BEA phase. SEM images (Fig. S2) of the four Hβ zeolites show uniform particles of ellipsoidal shape with the size of 0.2–0.5 μm. BET surface areas of Hβ-1, -2, -3 and -4 are 571, 629, 596 and 575 m^2/g respectively, according to nitrogen physical adsorption measurements as shown in Fig. S3, presenting slight differences from one another. ^{29}Si MAS NMR spectra of H-type samples (Fig. S4) depict different chemical environments of Si atoms, Q^3, Si(1Al) and three nonequivalent crystallographic Q^4 sites respectively [37]. The framework Si/Al ratios of Hβ zeolites (see Table 1) were calculated by deconvolutions of the ^{29}Si MAS NMR spectra according to the Loewenstein's rule [43]. ^{27}Al MAS NMR spectra (Fig. S5) showed that most of the Al atoms are in tetrahedral coordination state as the framework aluminum.

After dehydration at 400 °C under vacuum for 20 h, the four Hβ zeolites were characterized by ^1H MAS NMR spectroscopy (Fig. 1) for the quantification of their acid site densities. Thereinto, four peaks at 3.9, 2.5, 1.6 and 0.6 ppm can be distinguished on Hβ zeolites, which are attributed to bridge hydroxyl groups as the Brönsted acid sites, aluminum hydroxyl groups with hydrogen bonds effects, silicon hydroxyl groups and extra-framework aluminum hydroxyl groups, respectively [37,44,45]. For the assignment of the remaining broad line centered at 4.9 ppm, $^1H/^{27}Al$ TRAPDOR MAS NMR spectra were recorded and the spectra (Fig. S6) show that the signals at 4.9, 3.9, 2.5 and 0.6 ppm are strongly suppressed after ^{27}Al irradiation, indicating these peaks

Table 1
Si/Al ratios, Brönsted acid site densities of Hβ zeolites and quantification of MCP^+ cations.

Catalyst	Total Si/Al[a]	Framework Si/Al[b]	B-acid site concentration (mmol/g)	MCP^+ cations concentration[c] (mmol/g)	MCP^+ cations concentration/B-acid site concentration
Hβ-1	48	47	0.057	0.0039	~1/15
Hβ-2	36	43	0.092	0.0062	~1/15
Hβ-3	24	30	0.130	–	–
Hβ-4	13	24	0.162	0.0111	~1/15

[a] Determined with XRF.
[b] Determined with ^{29}Si MAS NMR.
[c] Methanol reaction under continuous-flow condition at 275 °C for 20 min.

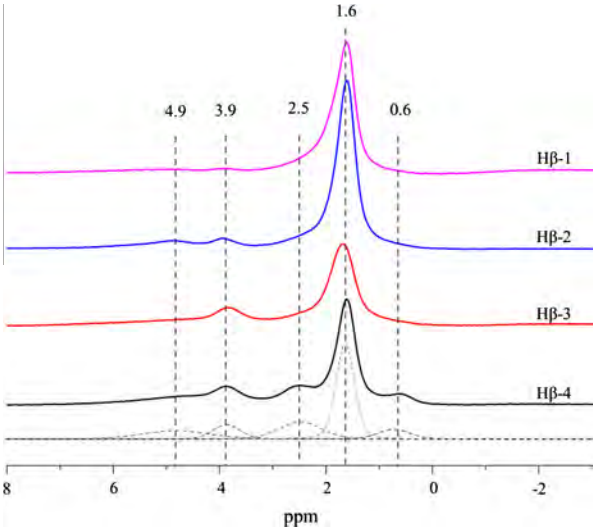


Fig. 1. ^{1}H MAS NMR spectra of Hβ zeolites.

are related to aluminum. So the peak at 4.9 ppm is associated with another kind of Brönsted acid site, not from template agent [37,46].

The Brönsted acid site concentrations have been determined by quantifying the bridge hydroxyl groups with their signal intensities, using hexamethylbenzene as the external standard. As displayed in Table 1, the Brönsted acid site densities of Hβ zeolites increase with the reduction of Si/Al ratios.

3.2. Conversion of $^{13}CH_3OH$ over Hβ zeolites under batch-like (BA) condition studied by ^{13}C MAS NMR

3.2.1. Conversion of adsorbed $^{13}CH_3OH$, DME and methoxyl groups without reactant atmosphere

Adsorption and reaction of methanol over Hβ zeolites generate adsorbed CH_3OH, DME and framework-bound methoxyl groups on the zeolite surface. In the spectra of ^{13}C MAS NMR of Hβ-4 (Fig. 2a), after heating the adsorbed methanol at 150 °C for 1 h in a sealed reactor and then evacuating it, the resonance peaks with chemical shifts at 50 ppm, 63 and 66 ppm, and 57 ppm correspond to the adsorbed methanol, dimethyl ether and surface methoxyl groups. ^{13}C CP/MAS NMR spectra (Fig. 2b) display the signals of adsorbed species with good resolution and two different adsorption states of DME, side-on (66 ppm) and end-on (63 ppm) [39,47,48], can be distinguished clearly. The other three catalysts, Hβ-1, -2 and -3 with relatively low Brönsted acid site concentration were also treated following the same procedure to form the surface adsorbed species and methoxyl groups for further transformation. Before the reaction, all the reactors were evacuated until the pressure is lower than 10^{-3} Pa and then heating the sealed reactor at 275 °C for 20 min to conduct the batch-like reaction. As shown in Fig. 3, the

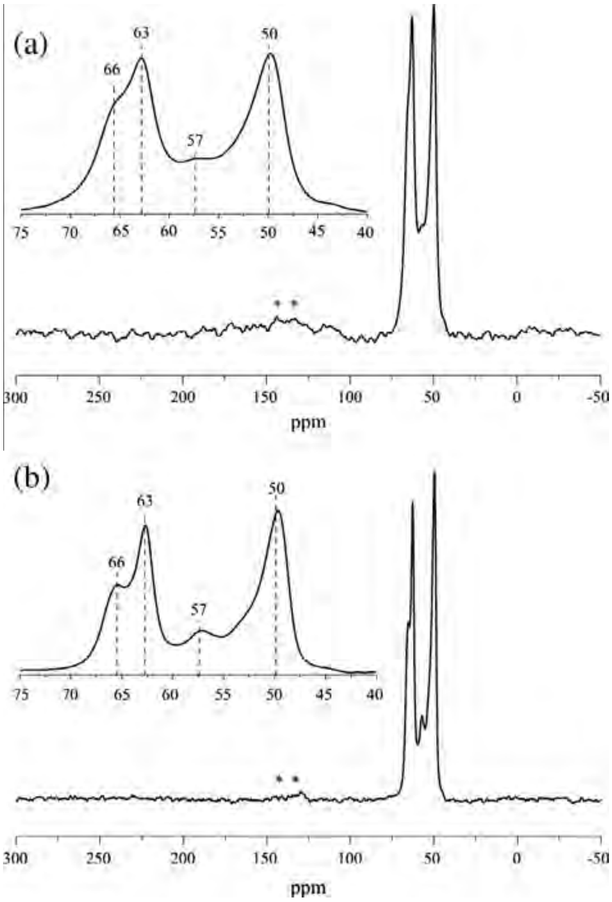


Fig. 2. ^{13}C MAS NMR spectra (a) and ^{13}C CP MAS NMR spectra (b) of adsorbed methanol, dimethyl ether and methoxyl groups on Hβ-4.

recorded spectra of the catalysts after reaction present no obvious variation, except the peak intensity increase of dimethyl ether. Over the catalysts with high acid site concentration, methanol conversion to dimethyl ether has been improved, but no hydrocarbons were generated based on the conversion of C_1 species (methanol, dimethyl ether and methoxyl groups) on the catalyst surface. The failure of hydrocarbon generation under this reaction condition indicates that the hydrocarbon formation from the reaction of adsorbed species or generated methoxyl groups on catalyst surface is quite difficult. C–C bond formation from surface methoxyl groups has been a controversial issue. Wang et al. suggested surface methoxyl groups are active species and initial hydrocarbon formation stems from the reaction of methoxyl groups [49–52]. Marcus and coworkers proposed an opposite view about the reactivity of framework-bound methoxyl groups in the direct mechanism of olefin synthesis based on the observation failure of H/D

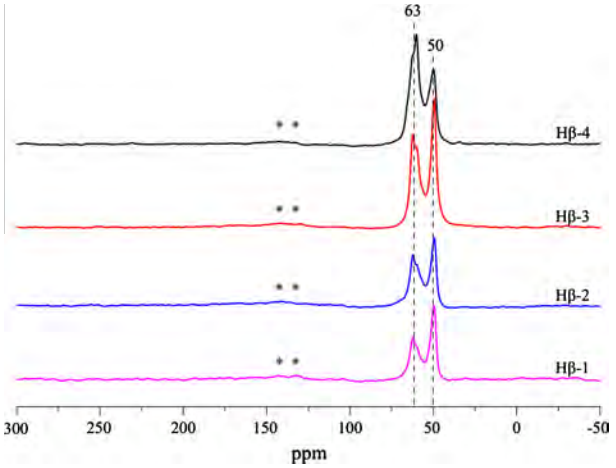


Fig. 3. ^{13}C MAS NMR spectra of Hβ zeolites after the batch-like reactions (BA) of adsorbed methanol, dimethyl ether and methoxyl groups at 275 °C for 20 min (spectra recorded at room temperature). *denotes spinning sideband.

exchange of framework-bound methoxyl groups at high temperatures [53,54].

The difficulty of methanol conversion only from the surface adsorbed C_1 species or methoxyl groups implies that under the batch-like reaction condition, reactant atmosphere is possibly important for MTH reaction. The participation of the reactants in the gas phase, such as methanol or dimethyl ether may be necessary for the MTH reaction.

3.2.2. $^{13}CH_3OH$ conversion with varied reactant atmosphere pressures and MCP^+ cations formation

In this section, after being fed $^{13}CH_3OH$ of 10 kPa at room temperature, the reactor was heated to reaction temperature of 275 °C and kept for 20 min to conduct the batch-like reaction under the reactant atmosphere.

As shown in the ^{13}C MAS NMR spectra measured after reaction (Fig. 4), for all the four Hβ catalysts, besides the signals from methanol at 50 ppm and DME at 63 ppm, the appearance of some resonance peaks in the range of aromatics, olefins and paraffins, indicates the occurrence of methanol or dimethyl ether transformation to hydrocarbon products. The signal at 122 ppm comes from ethene product and the signals at 142, 112 and 25 ppm are assigned to isobutene. The signal at 24 ppm, representing the isobutane formation, which can be easily formed by the hydrogen transfer reaction of isobutene, also appears in high intensity. The further identification of this product will be discussed in Section 3.2.5 in detail. Besides these volatile hydrocarbons formed and adsorbed on the catalyst surface, the generation of methyl-substituted aromatic products over the catalyst surface is also confirmed with the observation of the signals at 133 and 16 ppm. Comparing with the batch-like reaction of adsorbed methanol, dimethyl ether and surface methoxyl groups as described in Section 3.2.1, the existence of reactant in the atmosphere is greatly in favor of the conversion of methanol to hydrocarbon products. In a very early work of methanol conversion to hydrocarbons, Chang et al. reported that increasing the reactant partial pressure would improve the aromatization step in the reaction sequence [55]. Our previous work of chloromethane conversion studied by in situ FT-IR confirmed that with increasing pressure of reactant atmosphere in the quartz cell as the reactor, the hydrocarbon generation, including alkenes and aromatic products, was enhanced and the C_1 reactant in the gas phase was largely consumed at the same time [56]. Comparatively, under the identical reaction condition, almost no conversion occurred when chloromethane loading was very low over the catalyst. All these observations indicate that an effective formation of hydrocarbons from methanol over zeolite catalyst requires the participation of the reactant in the gas phase. The reaction of surface adsorbed methanol dimethyl ether and framework-bound methoxyl groups on Hβ zeolite catalyst is quite difficult.

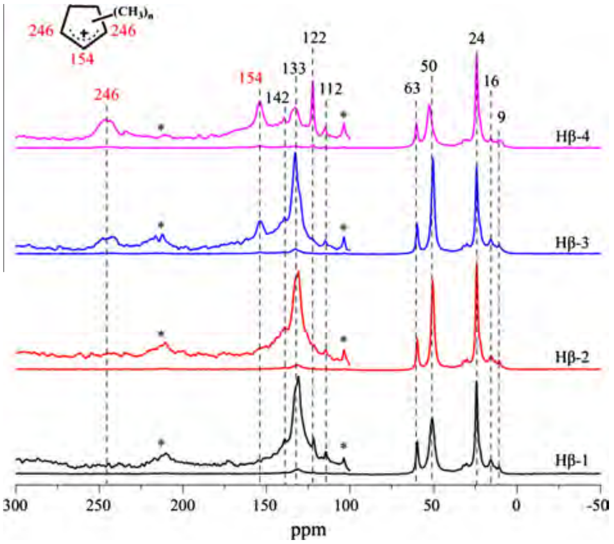


Fig. 4. ^{13}C MAS NMR spectra of Hβ zeolites after the batch-like reactions (BA) of methanol with reactant atmosphere of 10 kPa at 275 °C for 20 min (spectra recorded at room temperature). *denotes spinning sideband.

Comparing the spectra after the reaction over the four Hβ catalysts (Fig. 4), it is found that MTH reaction performance has been improved with the increase of Brönsted acid site densities of Hβ zeolites. The C_1 reactants, methanol and dimethyl ether on the catalyst surface are largely consumed over Hβ-4, which contains the highest Brönsted acid site density. And at the same time, more ethene is formed than that over the other Hβ zeolites with less Brönsted acid sites.

A very interesting observation is the appearances of two broad peaks of 246 and 154 ppm at the low field region in the ^{13}C spectra of Hβ-3 and Hβ-4, which should be assigned to the methyl-substituted cyclopentenyl (MCP^+) cations [32–34,57,58]. It is the first time of the capture and direct observation of MCP^+ cations over Hβ zeolite using only methanol as reactant with ^{13}C MAS NMR technique. It is demonstrated that MCP^+ cations are important reaction intermediates for methanol conversion over HZSM-5 and HSSZ-13 [32,59], thus may also work as the reaction intermediates for C–C bond assembly from methanol conversion over Hβ zeolites. It is worthy to note that the MCP^+ cations cannot be observed over the less acidic catalysts, Hβ-1 and Hβ-2, while some hydrocarbon products have been produced over them. This means that MCP^+ cations may also form over them, but MCP^+ cations cannot be detected due to the low concentration on the catalyst surface or consumed immediately once being formed over the catalysts. The appearance of MCP^+ cations over more acidic catalyst and their signal intensities increase with Brönsted acid site concentrations of the catalysts implies the function of Brönsted acid sites on the carbeniums formation and stabilization. The simultaneous observation of the MCP^+ cations on the catalyst and improved conversion of methanol reaction predict a positive correlation of the carbenium cations formation and hydrocarbon production over Hβ catalyst [19,32,59,60].

The loading of 10 kPa methanol in the reactor gives rise to the generation of hydrocarbon products and protonated products, and MCP^+ cations from methanol conversion. The influence of atmosphere pressure on the methanol reaction was studied by conducting a series of batch-like reactions over Hβ-4 at 275 °C with different atmosphere methanol pressures (5 kPa, 10 kPa, 20 kPa, 50 kPa and 80 kPa). The spectra measured after reaction for 20 min are displayed in Fig. 5. The reaction at low pressure methanol loading (5 kPa) generates relative fewer hydrocarbon products and MCP$^+$ cations. An increase of the methanol loading pressure to 10 kPa gives rise to the generation of hydrocarbon products with the signals in alkyl region (0–40 ppm) and aromatic region (120–140 ppm) and also the MCP$^+$ cations with the signals at 246 and 154 ppm. Further increase of the methanol loading pressure leads to more aromatics accumulation, but the intensities of MCP$^+$ cations signals show no change, implying that the carbenium ions formation is more possibly related to the available acid sites on the catalyst surface, on which they can be formed and stabilized.

3.2.3. Competitive adsorption over Hβ zeolite

Methanol conversion over Hβ zeolite under the reactant atmosphere exhibits improved hydrocarbon generation, while the capture of the MCP$^+$ cations is negatively affected by the adsorption of abundant reactant and generated hydrocarbon products. As shown in Fig. 6a, after the reaction conducted under methanol atmosphere of 20 kPa, the signals of adsorbed methanol at 50 ppm and dimethyl ether at 63 ppm appear with extremely high intensity and the formation of MCP$^+$ cations is hard to be detected. Evacuating the reactor at room temperature for 3 min (Fig. 6b), with the intensity decrease of the signals of methanol and dimethyl ether, the MCP$^+$ cations formation can be evidenced by the intensified signals at 246 and 154 ppm. This indicates that the competitive adsorption of methanol, dimethyl ether and generated hydrocarbons will influence the observation of protonated products, MCP$^+$ cations. Although they can be formed on the Brönsted acid site of Hβ zeolite, the comparative adsorption may cause the partial or complete proton loss and back to their neutral forms (Scheme 2). Prolonging the evacuation time at room temperature (Fig. 6c) or evacuating the batch-like reactor at relatively high temperature (40 °C, Fig. 6d), most of isobutane with chemical shift at 24 ppm can be removed from the catalyst. When the reactor is evacuated at 200 °C for 40 min (Fig. 6e), the adsorbed species, such as methanol and dimethyl ether with chemical shift of 50 and 63 ppm, leave the catalyst surface, but MCP$^+$ cations at 246 and 154 ppm and methylbenzene at 133 and 16 ppm can be reserved and intensified. The appearance of MCP$^+$ cations with high intensity after evacuation at 200 °C for 40 min means the high stability of the MCP$^+$ cations in the chemical environment of Hβ zeolite. The comparative study of carbenium ions observation under the condition with or without competitive adsorption further confirms the function of Brönsted acid sites in MCP$^+$ cations formation and stabilization which have been discussed in Section 3.2.2 and our previous work [32–34]. These results suggest that the participation of methanol or dimethyl ether in the gas phase may be necessary for the efficient production of hydrocarbons from methanol conversion, especially for the formation of MCP$^+$ cations, but the stay of the excess reactants or generated hydrocarbons on the catalyst surface would occupy Brönsted acid sites or disturb the charge distribution of MCP$^+$ cations and cause the deprotonation of these carbenium ions.

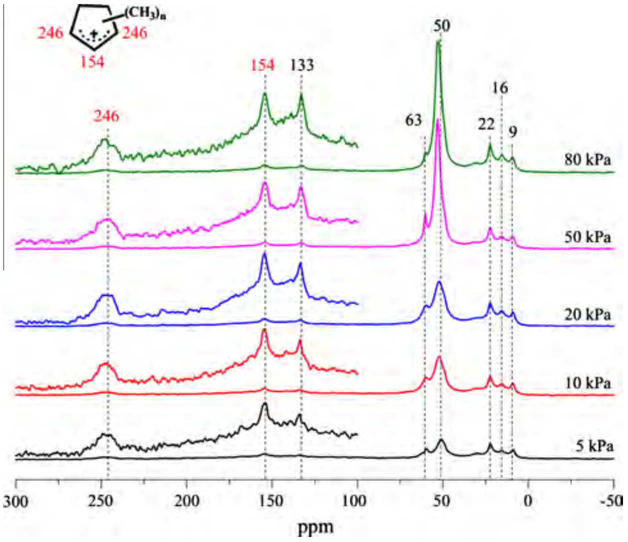


Fig. 5. ^{13}C MAS NMR spectra of Hβ-4 zeolite after the batch-like reactions (BA) of methanol with different reactant atmosphere pressures at 275 °C for 20 min (spectra recorded after evacuation at room temperature for 30 min).

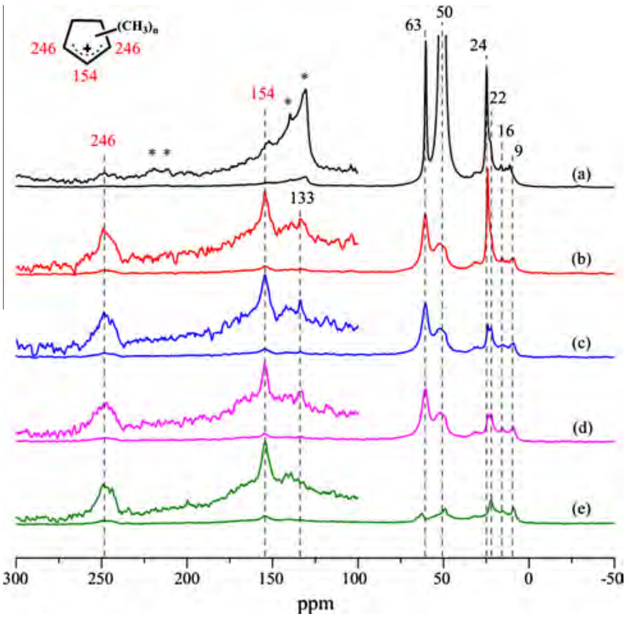
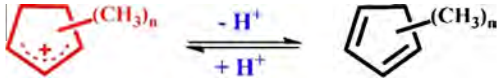


Fig. 6. ^{13}C MAS NMR spectra of Hβ-4 zeolite after the batch-like reactions (BA) of methanol at 275 °C for 20 min, spectra recorded at room temperature after various treatment: no evacuation (a), evacuation at RT for 3 min (b), evacuation at RT for 83 min (c), evacuation at 40 °C for 40 min (d), and evacuation at 200 °C for 40 min (e). *denotes spinning sideband.



Scheme 2. MCP$^+$ cations and their deprotonated forms, methylcyclopentadienes.

3.2.4. $^{13}CH_3OH$ conversion at different temperatures

Batch-like methanol conversion over Hβ catalysts was performed at temperature ranging from 250 to 325 °C. The ^{13}C MAS NMR spectra (Fig. 7) of $^{13}CH_3OH$ reaction are recorded after removing the volatile reactants and products with evacuation for a clarified observation of carbenium ions. When the reaction is performed at 250 °C, only the signals from adsorbed methanol at 50 ppm and dimethyl ether at 63 ppm appear, implying that the reaction temperature of 250 °C is too low to trigger the reaction of methanol conversion to hydrocarbons. For the reactions performed at temperature higher than 250 °C, reaction temperature has a great effect on methanol conversion. With temperature increase from 275 to 325 °C, the intensification of the signals in alkyl region (0–40 ppm) and aromatic region (120–140 ppm) indicates the improved generation of hydrocarbon products, especially

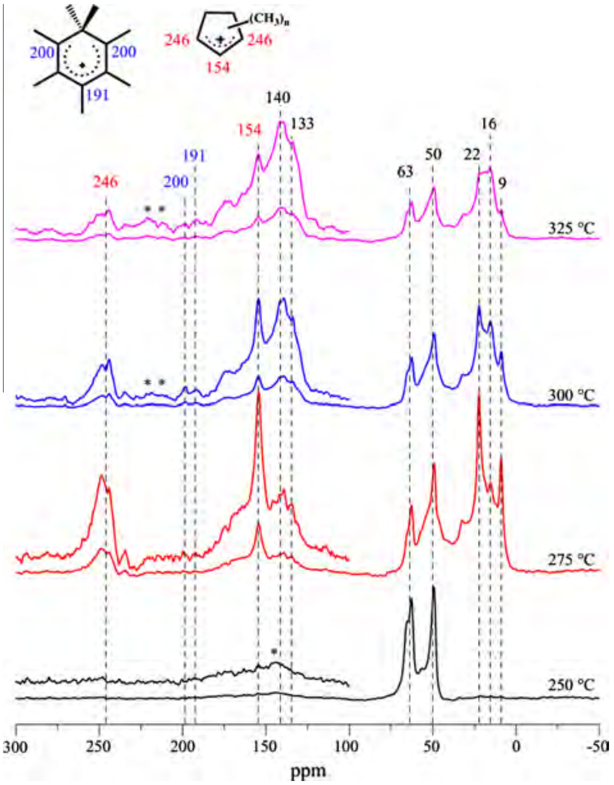


Fig. 7. ^{13}C MAS NMR spectra of Hβ-4 zeolite after the batch-like reactions (BA) of methanol at different reaction temperatures for 20 min, spectra recorded at room temperature after evacuation at 200 °C for 40 min. *denotes spinning sideband.

alkylbenzenes. It is worthy to note that the signal intensities of MCP^{+} cations at 246 and 154 ppm show different trends from those of aromatic hydrocarbon products at 133 and 140 ppm. With the appearance of a large amount aromatic hydrocarbon products as indicated by the strong peak at 133 and 140 ppm over the catalyst at 300 and 325 °C, the intensity of MCP^{+} cations is greatly lowered with increasing the temperature. This confirms the high reactivity of the carbenium ions as the important intermediates. The carbenium ions generation is accelerated at high temperature, but the further transformation causes the consumption of these active species, which makes the observation at relatively high temperature rather difficult. A new organic species with chemical shift at 200 and 191 ppm appears in the spectra after reaction at 300 °C, representing the formation of benzenium cation. Regarding the reported work of co-feeding methanol and benzene over Hβ, these signals are assigned to the heptamethylbenzenium cation, a very important carbenium ion as the hydrocarbon pool species [18].

3.2.5. GC–MS analysis of the retained compounds and the assignment of the signal at 24 ppm

In ^{13}C MAS NMR spectra of batch-like reactions catalyzed by Hβ zeolites, the signal at 24 ppm appears with very high intensity, indicating that it is a predominantly formed hydrocarbon product during methanol conversion. Since the intensity of this signal is reduced with evacuation at elevated temperature and prolonged time, this species can be desorbed as a volatile component among the generated products. For the identification of this species in batch-like reactions, ^{12}C-methanol conversion was conducted under the identical condition of ^{13}C-methanol reaction and the retained compounds in the catalysts were extracted with CH_2Cl_2 and CCl_4 separately. The GC–MS analysis of extracted organics is presented in Fig. S7.

The chromatogram shown in Fig. S7(a) indicates that among the generated hydrocarbons, isobutane appears as the main product and accounts for more than 50% of the extracted organics. Considering the characteristic ^{13}C MAS NMR peaks of tertiary carbon atom and primary carbon atom in isobutane are very close and both of them are around 24 ppm with less than 1 ppm discrepancy, the signal at 24 ppm in the spectra recorded after methanol conversion over Hβ is assigned to the adsorbed isobutane on the catalyst in combination with the analysis and identification of extracted organic compounds with GC–MS. This is consistent with the observations reported previously [49,61]. More detailed analysis of the C_1–C_6 hydrocarbon products presented in Fig. S7(b) indicates that besides isobutane, ethene, propene, *n*-butane, *n*-pentane and isopentane are also formed. Among the extracted aromatics products, methylbenzenes especially pentamethylbenzene and hexamethylbenzene are predominant.

3.3. Conversion of $^{13}CH_3OH$ over Hβ zeolites under continuous-flow (CF) condition studied by ^{13}C MAS NMR

In the batch-like reactions, methanol was fed into the reactor in advance at room temperature and then methanol conversion was performed in a sealed reactor. The reactant and its loading can be conveniently varied to study adsorption and reaction on the catalyst surface, while the whole reaction system encounters the reactant atmosphere variation with the extension of reaction time. For the case of continuous-flow reaction, the reactant of methanol is continuously fed to the catalyst bed to guarantee a stable reactant atmosphere. At the same time, the carrier gas for taking methanol vapor into reactor will remove the gaseous products from the catalyst surface, so the competitive adsorption of methanol, dimethyl ether, generated hydrocarbon product and water can be avoided to a great extent. Measuring the catalyst after continuous-flow reaction will disclose more information about the generation of carbenium ions as the intermediates or co-catalysts on the catalyst. This type of methanol reaction stands much closer to industrial MTH reaction. The observation of reaction intermediates under the real working condition is more important for the precise understanding of reaction mechanism.

3.3.1. ^{13}C MAS NMR spectra of continuous-flow $^{13}CH_3OH$ conversion over Hβ zeolites

Methanol conversion was performed at 275 °C over the three Hβ zeolites. The catalytic performances are detailed in Fig. S8. At 275 °C, an obvious induction period has been observed for methanol conversion over all the three catalysts. At TOS of 20 min, the conversions of methanol over Hβ zeolites all reach very high levels, implying active species, such as carbenium ions, also form with high concentrations according to our previous study on H-SSZ-13 zeolite [32]. For Hβ-4 sample, at TOS of 5 min, the predominated products among effluents are C_4 and C_5 alkane (Fig. S8(b)). It indicates that the H-unsaturated aromatic species are being formed on the catalyst, though the aromatics compounds cannot be detected in the effluents at this moment. After induction period, the C_4, C_5 alkane and polymethylbenzenes, especially hexamethylbenzene (HexaMB), are predominant in the effluents.

Fig. 8 shows the ^{13}C MAS NMR spectra of continuous-flow methanol reaction at 275 °C on Hβ catalysts with varied Brönsted acid site densities. Compared to the batch-like methanol conversion over Hβ zeolites (Fig. 4), more vivid reactions are presented for all the three Hβ catalysts. Hydrocarbon products, especially aromatic hydrocarbons are generated and presented in the spectra with extremely high signal intensities. Owing to the carrier gas flowing through the catalyst bed continuously, the short reactant/product–catalyst contact time causes the great reduction of the stay and adsorption of unreacted methanol, dimethyl ether,

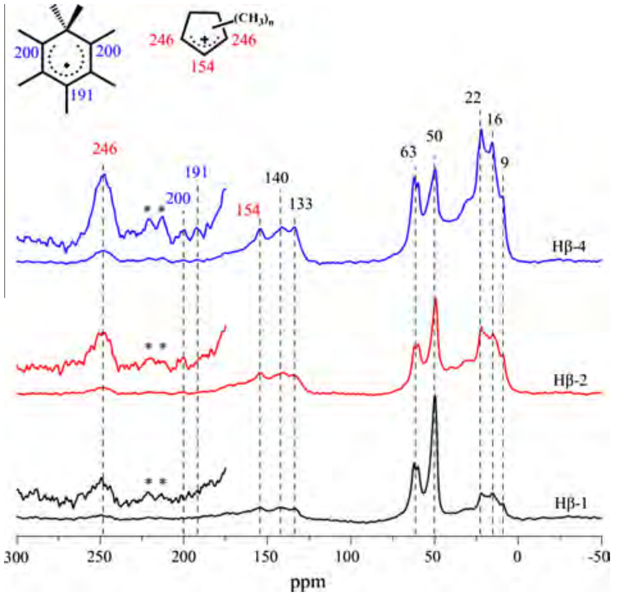


Fig. 8. ^{13}C MAS NMR spectra of Hβ zeolites after the continuous-flow (CF) reactions of methanol at 275 °C for 20 min (spectra recorded at room temperature). * denotes spinning sideband.

generated hydrocarbons and water on the Brönsted acid site of the zeolite catalyst. Therefore, methylcyclopentenyl (MCP$^+$) cations with characteristic chemical shifts of 246 and 154 ppm can be detected clearly on all the Hβ catalysts. Moreover, in the recorded spectrum of Hβ-4, polymethylbenzenium (PolyMB$^+$) cation with peaks at 200 and 191 ppm has also been observed, which has been assigned to be heptamethylbenzenium (heptaMB$^+$) cation by Song et al. with the co-reaction of ^{13}C-benzene and excess methanol over Hβ [18]. According to previous studies [18,61], heptaMB$^+$ cation is formed through a consecutive methylation of benzene or methylbenzene by the aid of the Brönsted acid sites; thus, methanol conversion under continuous-flow reaction condition, in which the reactant of methanol can be continuously fed to the catalyst bed, is in favor of the polymethylbenzene generation and the observation of heptaMB$^+$ cation.

3.3.2. Identification of carbenium ions formed in Hβ zeolite

For precise structure determination, $^{12}CH_3OH$ conversion was performed under identical reaction condition of $^{13}CH_3OH$ reaction as described in Section 2.3 and the retained organic species in Hβ-4 after reaction were analyzed by GC–MS, following the method introduced by Guisnet and coworkers [62–64]. As shown in the chromatogram in Fig. 9, methylbenzene and methylnaphthalene appear as the main components retained in Hβ-4. Two peaks at retention time of 11.6 and 13.0 min with mass-to-charge ratios (m/z) of 122 and 136 are identified by NIST11 library to be tetramethylcyclopentadiene (tetraMCP) and pentamethylcyclopentadiene (pentaMCP) respectively, indicating that the observed MCP$^+$ cations detected by ^{13}C MAS NMR are mainly pentamethylcyclopentenyl cation (pentaMCP$^+$) and tetramethylcyclopentenyl cation (tetraMCP$^+$). Another peak at retention time of 23.1 min with mass-to-charge ratio (m/z) of 176 is assigned to hexamethyl methylenecyclohexadiene (HMMC), consolidating the attribution that the PolyMB$^+$ cation detected by ^{13}C MAS NMR with chemical shifts of 200 and 191 ppm is heptamethylbenzenium (heptaMB$^+$) cation. Furthermore, GC–MS analysis has confirmed the formation of the methylcyclopentadiene and HMMC in Hβ-1 catalyst after methanol reaction under the batch-like condition as well (see Fig. S9). As shown in Fig. S9, tetraMCP$^+$, pentaMCP$^+$ and heptaMB$^+$ can be observed in Hβ-1 catalyst after batch-like reaction although they are not clearly detected by ^{13}C MAS NMR.

In order to confirm the adsorbed structures and NMR parameters of heptaMB$^+$ cation and pentaMCP$^+$ cation confined inside Hβ zeolite, the theoretical calculation was performed. The optimized results have illustrated that formed heptaMB$^+$ cation and pentaMCP$^+$ cation are perfectly accommodated inside the 12-membered ring and intersectional channel of Hβ. And then the ^{13}C chemical shifts of two confined cations were theoretically predicted by the GIPAW periodic methods, and this method has been extensively used for the NMR parameter calculations for the solid materials [42]. Taking the environment effect of the zeolite framework into account, such periodic method has been used to obtain the accurate chemical shift for the organic species inside Hβ zeolite [32]. With the consideration of the chemical environment of the Hβ zeolite with periodic method (for details see Section 2.5), the theoretically-predicted chemical shifts of heptaMB$^+$ cation (cation 5) in Hβ zeolite are 200 and 188 ppm (see Fig. 10(a)) which are very close to the experimental observation (200 and 191 ppm) as indicated in Figs. 7 and 8 and also in accordance with the previous studies carried out over Hβ catalyst [18]. Meanwhile, the calculated ^{13}C chemical shifts of ring carbon atoms of pentaMCP$^+$ cation (cation 6) confined inside the channel of Hβ zeolite are 244 and 152 ppm (see Fig. 10(b)), being also consistent with the experimental observation (246 and 154 ppm) in Figs. 4–8. Moreover, direct formation of pentaMCP$^+$ cation by adsorption of pentamethylcyclopentadiene molecules in Hβ zeolite also gives the close results with the appearance of the signals with chemical shifts of 247, 153 and 62/58 ppm [32]. During methanol conversion, the signal of methyl at 62/58 ppm is usually overlapped by the signals of dimethyl ether or methoxyl groups. Therefore, the formation of carbenium ions, heptaMB$^+$ cation and pentaMCP$^+$ cation during methanol conversion has been determined by combining ^{13}C MAS NMR, GC–MS analysis and theoretical prediction.

3.3.3. Quantification

For a precise estimation of important intermediates formation over Brönsted acid sites of Hβ catalysts with different acid site concentrations, the MCP$^+$ cations formed on the catalyst surface were quantified by integrating the area of the characteristic peak at 246 ppm in the ^{13}C MAS NMR spectra (Fig. 8) and the results are detailed in Table 1. Adamantane was used as the external standard for quantification. The ^{13}C MAS NMR spectra recorded after the continuous-flow methanol conversion over Hβ catalysts demonstrate that more carbenium ions formation and enhanced hydrocarbon product generation can be realized over Hβ catalysts with relatively high acid site concentration. The MCP$^+$ cations concentrations are 0.0039, 0.0062 and 0.0111 mmol/g for the catalysts of Hβ-1, -2 and -4, respectively. If considering the difference of acid site concentrations among the three catalysts, it is interesting to note that the number of Brönsted acid sites required for one carbenium formation is close among the three Hβ zeolites, i.e. one MCP$^+$ cation formation requires the catalysis and stabilization from about 15 Brönsted acid sites over all the three Hβ zeolites. Even with varied acid site concentrations, the three Hβ zeolites with different Si/Al ratios possess close capacity for MCP$^+$ cations formation. In principle, one MCP$^+$ cation requires only one Brönsted acid site to be stabilized. The excess acid sites may be dominated by other adsorbed organic species, such as methanol, dimethyl ether, methoxyl groups, and other carbenium ions which cannot be captured by NMR. And the close capacity for MCP$^+$ cations formation and stabilization over all the Hβ zeolites implies the close Brönsted acid properties including distribution and strength of all the three Hβ zeolites, which presented the close reactivity of methanol conversion catalyzed by each Brönsted acid site.

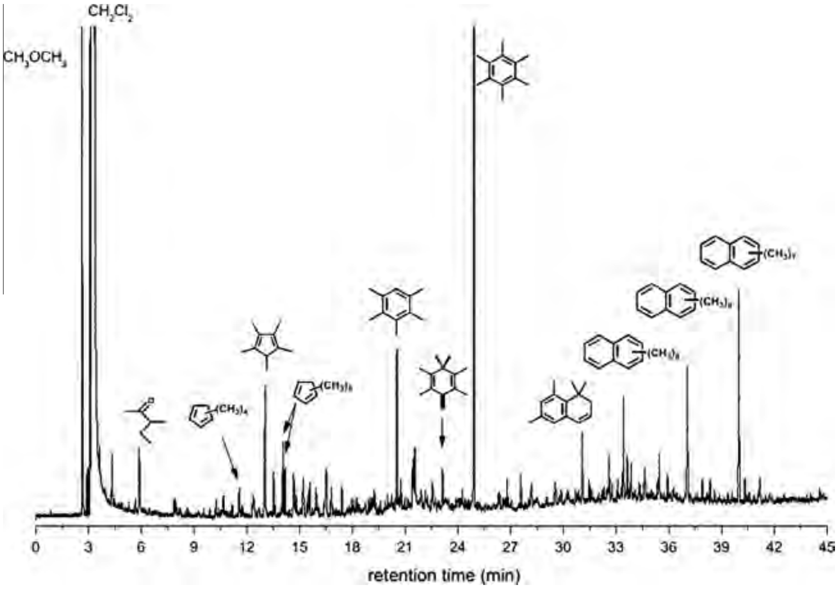


Fig. 9. GC–MS chromatogram of the organic species retained in Hβ-4 after continuous-flow methanol conversion at 275 °C for 20 min. After the reaction, the reactor was quenched with liquid nitrogen and the catalyst was diluted in HF solution and treated with CH_2Cl_2 to extract the organic species for analysis.

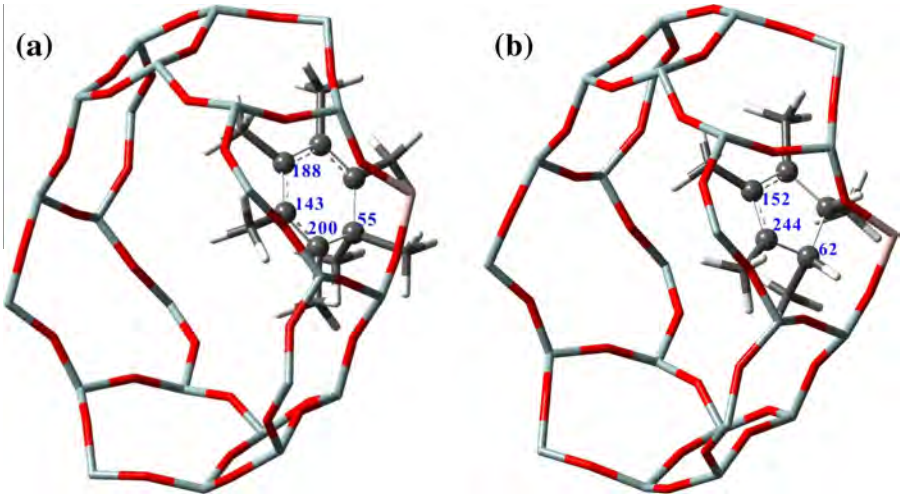


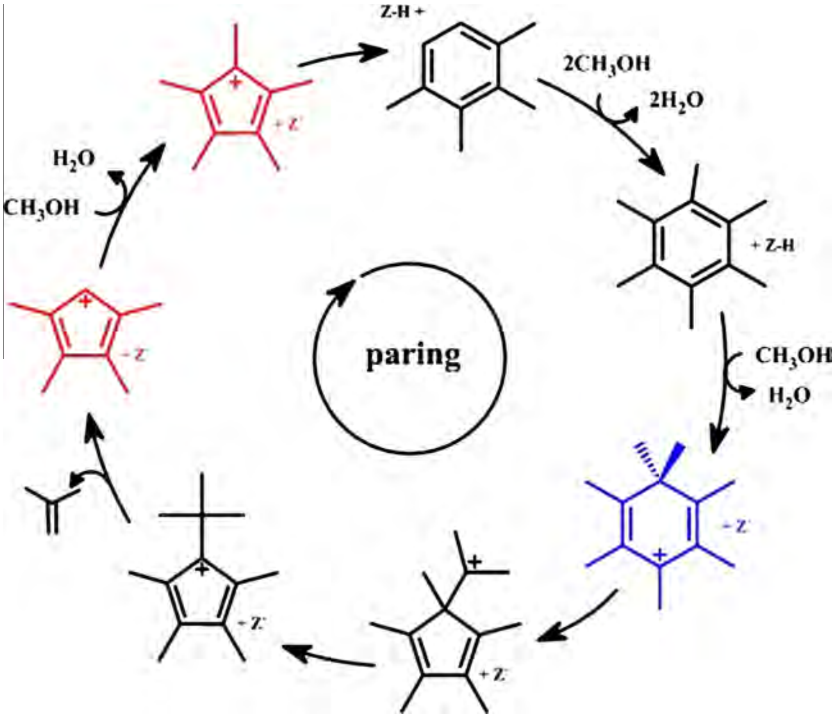
Fig. 10. Theoretically predicted chemical shifts of heptaMB$^+$ cation (a) and pentaMCP$^+$ cation (b) confined in Hβ zeolite.

The quantification of heptaMB$^+$ cation is difficult due to the much lower intensity of its characteristic signals in the ^{13}C MAS NMR spectra, but the qualitative analysis shows the similar relationship between heptaMB$^+$ cation observation and Brönsted acid site concentration as MCP$^+$ cations formation over Hβ zeolites under continuous-flow condition.

3.4. Catalytic cycle

Two different reaction routes have been proposed for the conversion of methanol to olefins product with the involvement of carbenium ions as the reaction intermediates. One is named side-chain mechanism that involves exo-cyclic methylation of heptaMB$^+$ cation, HMMC, and subsequent elimination of alkene products [24,25,65]. The other is named paring mechanism which was firstly described by Sullivan et al. [22] and involves the contraction of polymethylbenzenium cations and the expansion of methylcyclopentenyl cations [22,59,61]. Sassi et al. studied the reaction of ^{13}C-methanol and ^{12}C-methylbenzenes at 450 °C and suggested that side-chain mechanism was the dominating route for olefin formation over Hβ zeolite [24,25]. Based on the observation of large amount of alkene products containing the ^{12}C atoms from benzene ring in the co-reaction of ^{12}C-benzene and ^{13}C-methanol, paring mechanism was proposed by Bjørgen et al. to explain isobutene formation over Hβ zeolite at relatively low reaction temperature [61,66]. The two reaction mechanism proposals aimed to describe the generation of the alkene product mainly-formed over Hβ zeolite in each study. In the reaction performed by Sassi et al., the main hydrocarbon product was propene at 350–450 °C and isobutene generation was suppressed in this temperature range [24,25]. In the work of Bjørgen et al., the main hydrocarbon product was isobutane at reaction temperature lower than 330 °C [61,66].

In the present work, after continuous-flow methanol conversion at 275 °C, as shown in the chromatogram in Fig. S8(c), isobutane is produced as the main product, which is consistent with the obser-



Scheme 3. Proposed reaction route of paring mechanism for isobutene formation on Hβ zeolite.

vation in the work conducted by Bjørgen et al. [61,66]. This also corresponds to the much intensified signal of isobutane at 24 ppm in the ^{13}C MAS NMR spectra recorded after both batch-like and continuous-flow reactions. Isobutane is formed from the H-transfer reaction of isobutene as a secondary product of methanol reaction. Based on the observation and identification of the carbenium ions, heptaMB$^+$ and MCP$^+$ cations, a catalytic cycle (Scheme 3) is proposed, in which isobutene is generated via the reaction route of paring mechanism with the involvement of tetraMCP$^+$, pentaMCP$^+$ and heptaMB$^+$ cations as the important intermediates. The observation of important intermediates of carbenium ions by ^{13}C MAS NMR spectroscopy gives the direct and strong evidences of the feasibility of paring mechanism during methanol conversion over Hβ zeolite at temperature below 325 °C.

4. Conclusions

Batch-like and continuous-flow methanol conversions over Hβ zeolites have been systemically investigated with ^{13}C MAS NMR spectroscopy. For the first time, the important reaction intermediates, heptamethylbenzenium (heptaMB$^+$) cation and methylcyclopentenyl (MCP$^+$) cations have been directly observed during methanol conversion by the aid of solid-state NMR technique. Brönsted acid sites of Hβ zeolite catalysts play important roles in carbenium ions formation and observation. Methanol to hydrocarbons reaction and carbenium ions formation have been promoted by the usage of the Hβ catalysts with high acid site concentration under both batch-like and continuous-flow reaction conditions. The batch-like methanol reactions performed with varied reactant atmosphere pressures confirm that the participation of methanol or dimethyl ether in the gas phase will improve the methanol conversion to hydrocarbons and the generation of MCP$^+$ ions on the Brönsted acid sites of the catalyst. The competitive adsorption of methanol, dimethyl ether and generated hydrocarbons on the catalyst surface causes the deprotonation of the formed carbeniums. Evacuating after batch-like reaction or performing the reaction under continuous-flow condition, in which these competitive adsorbates can be removed immediately once being formed, will be an optimized strategy for carbeniums capture and observation. Compared to batch-like reaction, both the MCP$^+$ and heptaMB$^+$ cations are more easily captured in continuous-flow methanol reaction over the same catalyst and at the same reaction temperature. This is due to the participation of continuously-fed methanol in the reaction in favor of carbeniums formation and also stems from the reduction of severe interference from competitive adsorption as occurs in batch-like reactions. The identification of heptaMB$^+$ and MCP$^+$ (tetraMCP$^+$ and pentaMCP$^+$) cations is consolidated by the observation of their deprotonated products among the retrained compounds in the catalysts. The quantification results of the MCP$^+$ cations formation over the catalysts indicate that the Brönsted acid sites in different Hβ zeolites with varied acid densities possess close capacity for MCP$^+$ cations formation and one MCP$^+$ cation formation requires the catalysis and stabilization from about 15 Brönsted acid sites for all the three Hβ zeolites in continuous-flow reactions. Based on the carbenium ions observation and determination, a catalytic cycle is proposed, in which isobutene is generated via the reaction route of paring mechanism with the involvement of tetraMCP$^+$, pentaMCP$^+$ and heptaMB$^+$ cations as the important intermediates.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (Nos. 21473182, 21273230, 21273005, 21210005, 21173255, 21176255 and 21103180), the Youth Innovation Promotion Association of the Chinese Academy of Sciences and the Ministry of Science and Technology of China through the National Basic Research Program of China (No. 2012CB215002).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.12.007.

References

[1] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[2] C.D. Chang, Catal. Rev. – Sci. Eng. 26 (1984) 323.
[3] M. Stocker, Micropor. Mesopor. Mater. 29 (1999) 3.
[4] U. Olsbye, S. Svelle, M. Bjorgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Angew. Chem. Int. Ed. 51 (2012) 5810.
[5] Z.M. Liu, Y. Qi, Bull. Chin. Acad. Sci. 21 (2006) 406.
[6] P. Tian, Y.X. Wei, M. Ye, Z.M. Liu, ACS Catal. 5 (2015) 1922.
[7] N.Y. Chen, W.J. Reagan, J. Catal. 59 (1979) 123.
[8] Y. Ono, T. Mori, J. Chem. Soc. Farad. Trans. 1 (77) (1981) 2209.
[9] G.J. Hutchings, F. Gottschalk, M.V.M. Hall, R. Hunter, J. Chem. Soc. Farad. Trans. 1 (83) (1987) 571.
[10] G.A. Olah, Pure Appl. Chem. 53 (1981) 201.
[11] D. Kagi, J. Catal. 69 (1981) 242.
[12] C.D. Chang, J. Catal. 69 (1981) 244.
[13] I.M. Dahl, S. Kolboe, Catal. Lett. 20 (1993) 329.
[14] I.M. Dahl, S. Kolboe, J. Catal. 149 (1994) 458.
[15] I.M. Dahl, S. Kolboe, J. Catal. 161 (1996) 304.
[16] X.Y. Sun, S. Mueller, H. Shi, G.L. Haller, M. Sanchez-Sanchez, A.C. van Veen, J.A. Lercher, J. Catal. 314 (2014) 21.
[17] X.Y. Sun, S. Mueller, Y. Liu, H. Shi, G.L. Haller, M. Sanchez-Sanchez, A.C. van Veen, J.A. Lercher, J. Catal. 317 (2014) 185.
[18] W.G. Song, J.B. Nicholas, A. Sassi, J.F. Haw, Catal. Lett. 81 (2002) 49.
[19] J.F. Haw, J.B. Nicholas, W.G. Song, F. Deng, Z.K. Wang, T. Xu, C.S. Heneghan, J. Am. Chem. Soc. 122 (2000) 4763.
[20] W.G. Song, J.B. Nicholas, J.F. Haw, J. Phys. Chem. B 105 (2001) 4317.
[21] T. Xu, D.H. Barich, P.W. Goguen, W.G. Song, Z.K. Wang, J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc. 120 (1998) 4025.
[22] R.F. Sullivan, C.J. Egan, G.E. Langlois, R.P. Sieg, J. Am. Chem. Soc. 83 (1961) 1156.
[23] D. Lesthaeghe, A. Horre, M. Waroquier, G.B. Marin, V. Van Speybroeck, Chem. Eur. J. 15 (2009) 10803.
[24] A. Sassi, M.A. Wildman, H.J. Ahn, P. Prasad, J.B. Nicholas, J.F. Haw, J. Phys. Chem. B 106 (2002) 2294.
[25] A. Sassi, M.A. Wildman, J.F. Haw, J. Phys. Chem. B 106 (2002) 8768.
[26] G.A. Olah, P.R. Clifford, Y. Halpern, R.G. Johanson, J. Am. Chem. Soc. 93 (1971) 4219.
[27] G.A. Olah, G. Liang, J. Am. Chem. Soc. 94 (1972) 6434.
[28] G.A. Olah, G. Liang, Y.K. Mo, J. Am. Chem. Soc. 94 (1972) 3544.
[29] G.A. Olah, R.J. Spear, G. Messina, P.W. Westerman, J. Am. Chem. Soc. 97 (1975) 4051.
[30] J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc. 120 (1998) 11804.
[31] J.F. Haw, J.B. Nicholas, T. Xu, L.W. Beck, D.B. Ferguson, Acc. Chem. Res. 29 (1996) 259.
[32] S.T. Xu, A.M. Zheng, Y.X. Wei, J.R. Chen, J.Z. Li, Y.Y. Chu, M.Z. Zhang, Q.Y. Wang, Y. Zhou, J.B. Wang, F. Deng, Z.M. Liu, Angew. Chem. Int. Ed. 52 (2013) 11564.
[33] J.Z. Li, Y.X. Wei, J.R. Chen, P. Tian, X. Su, S.T. Xu, Y. Qi, Q.Y. Wang, Y. Zhou, Y.L. He, Z.M. Liu, J. Am. Chem. Soc. 134 (2012) 836.
[34] J.Z. Li, Y.X. Wei, J.R. Chen, S.T. Xu, P. Tian, X.F. Yang, B. Li, J.B. Wang, Z.M. Liu, ACS Catal. 5 (2015) 661.
[35] Q.Y. Wang, Y.X. Wei, S.T. Xu, M.Z. Zhang, S.H. Meng, D. Fan, Y. Qi, J.Z. Li, Z.X. Yu, C.Y. Yuan, Y.L. He, S.L. Xu, J.R. Chen, J.B. Wang, B.L. Su, Z.M. Liu, Chin. J. Catal. 35 (2014) 1727.
[36] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Magn. Reson. Chem. 40 (2002) 70.
[37] X.J. Li, W.P. Zhang, S.L. Liu, L.Y. Xu, X.W. Han, X.H. Bao, J. Catal. 250 (2007) 55.
[38] C.P. Grey, A.J. Vega, J. Am. Chem. Soc. 117 (1995) 8232.
[39] W. Wang, M. Seiler, M. Hunger, J. Phys. Chem. B 105 (2001) 12553.
[40] J.B. Wang, J.Z. Li, S.T. Xu, Y.C. Zhi, Y.X. Wei, Y.L. He, J.R. Chen, M.Z. Zhang, Q.Y. Wang, W.N. Zhang, X.Q. Wu, X.W. Guo, Z.M. Liu, Chin. J. Catal. 36 (2015) 1392.
[41] X. Wu, M.C. Vargas, S. Nayak, V. Lotrich, G. Scoles, J. Chem. Phys. 115 (2001) 8748.
[42] M. Profeta, F. Mauri, C.J. Pickard, J. Am. Chem. Soc. 125 (2003) 541.
[43] W. Loewenstein, Am. Mineral. 39 (1954) 92.
[44] W.P. Zhang, M.Y. Sun, R. Prins, J. Phys. Chem. B 106 (2002) 11805.
[45] M. Hunger, Catal. Rev. – Sci. Eng. 39 (1997) 345.
[46] X.J. Li, W.P. Zhang, S.L. Liu, X.W. Han, L.Y. Xu, X.H. Bao, J. Mol. Catal. A: Chem. 250 (2006) 94.
[47] I.I. Ivanova, A. Corma, J. Phys. Chem. B 101 (1997) 547.
[48] S.R. Blaszkowski, R.A. vanSanten, J. Am. Chem. Soc. 119 (1997) 5020.
[49] W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc. 125 (2003) 15260.
[50] W. Wang, Y.J. Jiang, M. Hunger, Catal. Today 113 (2006) 102.
[51] Y.J. Jiang, M. Hunger, W. Wang, J. Am. Chem. Soc. 128 (2006) 11679.
[52] Y.J. Jiang, W. Wang, V.R.R. Marthala, J. Huang, B. Sulikowski, M. Hunger, J. Catal. 238 (2006) 21.
[53] D.M. Marcus, K.A. McLachlan, M.A. Wildman, J.O. Ehresmann, P.W. Kletnieks, J. F. Haw, Angew. Chem. Int. Ed. 45 (2006) 3133.
[54] D.M. Marcus, M.J. Hayman, Y.M. Blau, D.R. Guenther, J.O. Ehresmann, P.W. Kletnieks, J.F. Haw, Angew. Chem. Int. Ed. 45 (2006) 1933.
[55] C.D. Chang, W.H. Lang, R.L. Smith, J. Catal. 56 (1979) 169.
[56] Y.X. Wei, D.Z. Zhang, Z.M. Liu, B.L. Su, J. Catal. 238 (2006) 46.
[57] C. Wang, Y.Y. Chu, A.M. Zheng, J. Xu, Q. Wang, P. Gao, G.D. Qi, Y.J. Gong, F. Deng, Chem. Eur. J. 20 (2014) 12432.
[58] P.W. Goguen, T. Xu, D.H. Barich, T.W. Skloss, W.G. Song, Z.K. Wang, J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc. 120 (1998) 2650.
[59] D.M. McCann, D. Lesthaeghe, P.W. Kletnieks, D.R. Guenther, M.J. Hayman, V. Van Speybroeck, M. Waroquier, J.F. Haw, Angew. Chem. Int. Ed. 47 (2008) 5179.
[60] M.J. Wulfers, F.C. Jentoft, ACS Catal. 4 (2014) 3521.
[61] M. Bjørgen, U. Olsbye, D. Petersen, S. Kolboe, J. Catal. 221 (2004) 1.
[62] M. Guisnet, L. Costa, F.R. Ribeiro, J. Mol. Catal. A: Chem. 305 (2009) 69.
[63] M. Guisnet, J. Mol. Catal. A: Chem. 182 (2002) 367.
[64] P. Magnoux, F. Machado, M. Guisnet, W.C. Conner, H. Schulz, N.A. Prokudina, S. Csicsery, P.G. Menon, J.P. Fraissard, Stud. Surf. Sci. Catal. 75 (1993) 435.
[65] B. Arstad, J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc. 126 (2004) 2991.
[66] M. Bjørgen, U. Olsbye, S. Svelle, S. Kolboe, Catal. Lett. 93 (2004) 37.