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A brand new zeolite catalyst for carbonylation reaction †

Xiaobo Feng,[a] Jie Yao,[a] Hangjie Li,[a] Yuan Fang,[a] Yoshiharu Yoneyama,[a] Guohui Yang*[ab] and Noritatsu Tsubaki *[a]

Carbonylation is an effective way to introduce carbonyl group into organic chemicals. But the known zeolite candidates for carbonylation are in single digits. Herein, we discovered a new zeolite of EU-12 that shows excellent catalytic performance for carbonylation reaction, inserting carbonyl into dimethyl ether (DME) to produce methyl acetate (MA). This finding added a brand new zeolite to the solid catalysts family for carbonylation reaction.

Inserting carbonyl group into organic chemicals to produce carbonyl-containing chemical compounds is a crucial process in chemistry.[1] The catalysts used for carbonylation are usually homogeneous or heterogeneous.[2] Zeolite is one promising catalyst family for carbonylation reaction because of its advantages of green, easy separation from the products and the ability of regeneration. But the number of zeolite candidates in this catalyst family is fairly low. Until now, only Y, MOR, ZSM-5 and ZSM-35 zeolites, are discovered to exhibit their catalytic performance for carbonylation reactions. And they are used for carbonylation of methanol or DME to produce acetic acid or MA.[3] The traditional catalysts for carbonylation reaction usually use halide complex or Rh/Ir organometallic complexes those are toxic to human health and harmful to environment.[4] The zeolite catalysts of Y, ZSM-5 and MOR were first discovered by Fujimoto *et al.* in 1984 for methanol carbonylation. Iglesia *et al.* investigated a series of zeolite catalysts and proved that only MOR and ZSM-35 zeolite possess carbonylation ability to convert DME into MA at relatively low reaction temperatures (423-513K). However, both two zeolites are suffered from rapid deactivation because their channels are easily blocked by the deposition of coke species.[3]

Discovering more zeolite candidates for carbonylation reaction is very crucial to organic chemicals synthesis through introducing carbonyl group via heterogeneous catalysis approach.
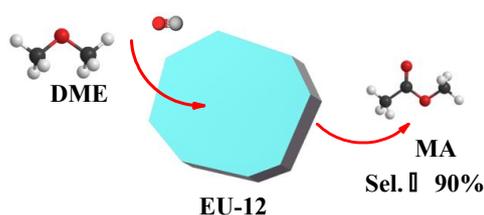
Scheme 1 Illustration for the DME carbonylation over the EU-12 zeolite to produce MA.

Herein, in this report, we found a new zeolite of EU-12 that has excellent carbonylation performance for DME conversion to produce MA, as illustrated by the Scheme 1. Compared to MOR and ZSM-35, EU-12 exhibits better stability and higher MA selectivity. Possibly, EU-12 will be a more promising zeolite candidate for DME carbonylation to MA.

EU-12, an Endinburgh University-twelve (ETL) type zeolite, was first reported by Araya *et al.* in 1986 as a new ETL-type zeolite.[5] EU-12 zeolite has an unique framework topology that contains two dimensional types of straight 8-MR (4.6 ×2.8 and 5.0 ×2.7 Å) channels along c axis. The smaller one connects with the sinusoidal 8-ring (4.8 ×3.3 Å) channel along a axis, while the other larger one links to sinusoidal channels by sharing 8-rings (4.8 ×2.6 Å) in the ac plane.[6] The EU-12 zeolite was known to exhibit unique acid-catalytic properties and showed an excellent ethane selectivity as shape-selective catalyst for low-temperature dehydration of ethanol.[6] But it is not found its ability for carbonylation reaction until now. The special feature of EU-12 zeolite has attracted our attentions because of its special 8-MR channels, which suggests its potential ability for preferential CO adsorption with methoxyl species to generate acetyl group.[7] These characteristics predicate EU-12 zeolite a potential candidate for carbonylation reaction. However, unfortunately, only the original synthesis patent and the zeolite structure description have been reported for EU-12 zeolite. As described by Bae *et al.*, the preparation of EU-12 zeolite was very rigorous to both Al and Rb contents in the mixture composition.[6] When the $Rb_2O/ (Rb_2O+Na_2O)$ ratio in the gel was fixed at 0.7, the SiO_2/Al_2O_3 ratio in the final EU-12 zeolite sample was found to be 20 only. In this report, we used choline chloride (ChCl) as an

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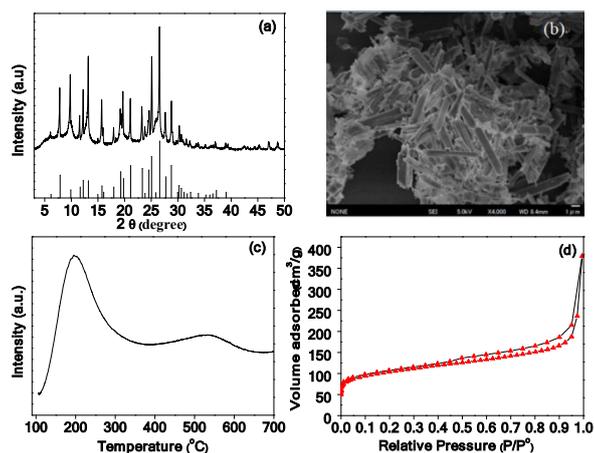
Fig.1 (a) The XRD patterns of EU-12 zeolite; (b) the SEM image of EU-12 zeolite; (c) the NH_3-TPD profile of EU-12 zeolite; (d) the nitrogen adsorption-desorption isotherm of EU-12 zeolite.

organic structure-directing agent (OSDA) to prepare EU-12 zeolite.

As shown in Fig. 1a, EU-12 zeolite structure was identified by comparing the diffraction peaks of sample with the standard data in the literature (PDF: 00-048-0733).[6] All of the diffraction peaks belonged to the EU-12 zeolite. The thermogravimetric (TG) curve (Fig. S1, ESI†) of the fresh EU-12 sample without calcination showed an exothermic loss (about 14.6%) around 600 °C. The decomposition of organic compounds at this high temperature indicated that the EU-12 zeolite contained many channels smaller than 10-rings.[6] As exhibited by the sample SEM image in Fig. 1b, EU-12 zeolite presented a typical morphology as a bar-shape with about 0.5 μm in diameter and 3 μm in length. For the acidic properties analysis of the EU-12 sample, two major desorption peaks at 200 °C and 530 °C were found in its NH_3-TPD curve (Fig.1c). These two peaks can be assigned to weak acid sites or extra framework aluminium (EFAl) and strong (Brønsted and/or Lewis) acid sites, respectively.[8] The acid sites amount was summarized and given in Table S1, ESI†. The N_2 adsorption-desorption isotherm (Fig. 1d) of EU-12 zeolite exhibited a type-Ⅰ isotherm, suggesting its classic microporous structure. The structure features and textural properties of EU-12 zeolite were also illustrated in Table S1, ESI†. The EU-12 zeolite had a surface area of 330.2 m^2/g and a micropore volume of 0.588 cm^3/g. XRF analysis suggested that the Si/Al was 8.3. Two major peaks centered at -112 and -105 ppm and a less intense peak at -99 ppm were found in the ^{29}Si MAS NMR spectra (Fig. S2a, ESI†), which correspond to the Si(0Al), Si(1Al) and Si-OH species, respectively.[9] This result indicated that the Si atoms in EU-12 zeolite were mainly at the Si(0Al) and Si(1Al) sites. In the ^{27}Al MAS NMR (Fig. S2b, ESI†) spectra, the big peak at 51 ppm was assigned to tetrahedrally coordinated framework Al (Al ^{IV}) while the small peak at near 0 ppm was attributed to octahedrally coordinated EFAl.[9] The details about preparation of EU-12 zeolite, the characterization, and the experimental process were summarized in the ESI†.

We demonstrated the high stability and extraordinary selecti-

-vity of H-type of EU-12 (HEU-12) zeolite for carbonylation reaction, in which DME was used as the start material to produce MA. Fig. 2 displayed the catalytic performance of the HEU-12 zeolite for DME carbonylation as a function of time on stream (TOS) from 220 °C to 240 °C at 1.5 MPa. It seems that the HEU-12 zeolite shows better catalytic performance for DME carbonylation at 220 °C. The DME conversion is more stable without obvious deactivation (Fig. 2a), and MA selectivity is always higher than 90% with only few methanol and hydrocarbons as by-products (Fig. 2b). Higher reaction temperature, like 230 °C and 240 °C, leads to the rapid deactivation of HEU-12, as well as lower MA selectivity and more by-products.

On the by-products, a small amount of CO_2 was mainly ascribed to water-gas-shift (WGS) reaction and CH_4 was attributed to the decomposition of surface methoxyl groups and DME, as verified by previous research.[10] Additionally, it was reported that DME and the formed MA could be decomposed into CO_2 and CH_4 on the acids sites of zeolite above 230 °C. Methanol was the main by-product during the 10 h test, which was attributed to a quasi-equilibrated reaction of DME with acidic protons (mainly Brønsted acid).[8] It was found that, under the reaction conditions studied here, the deactivation rate and the selectivity of major by-products (methanol and CO_2) increased slightly with the increase of reaction temperature, though higher catalytic activity was obtained at 240 °C. Fig. S3 illustrated the deactivation rate constants (K_d), calculated from the MA formation rate (R_{MA}).[11] The K_d value was associated with the production of methanol and hydrocarbons in the reaction process. These results demonstrated that higher reaction temperature realized better DME conversion, but at the same time leaded to homologation and oligomerization side-reactions to form other hydrocarbons and coke. The coke contents in the spent HEU-12 zeolites were detected using TG analysis (Fig. S4, ESI†).
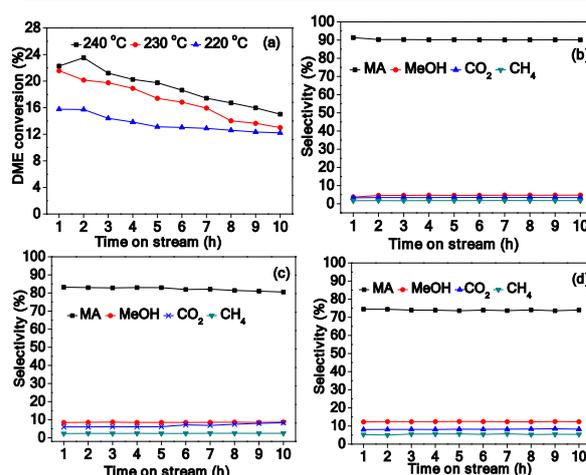
Fig. 2 (a) The conversion of DME at 240 °C, 230 °C and 220 °C on HEU-12 zeolite; (b) the product selectivity at 220 °C; (c) 230 °C and (d) 240 °C. Reaction conditions: P=1.5 MPa, feed gas: 3.03% Ar/4.13 DME/92.84 CO, flow rate =20 mL/min, weight $_{(zeolite)}$ =0.5 g, MeOH: methanol.

In order to investigate the catalytic lifetime of HEU-12 zeolite, further reaction test as long as 50 h was carried out at the optimized condition of 220 °C and 1.5 MPa (Fig. 4a). The conversion of DME decreased form 15.7% at 2 h to 10.0% at 30 h and then became stable. Moreover, the selectivity of MA was kept above 90% during the total reaction process. This result confirmed that the stability of HEU-12 is better than that of HMOR and HZSM-35 under the same reaction condition (Fig. S 5a, ESI†). Other reference zeolites of Y, Beta, and ZSM-5 exhibited a rapid deactivation and zero MA selectivity (Fig. S5b, ESI†). These results indicate that the zeolite with only 10-MR or 12-MR but no 8-MR, such as Beta, Y, and ZSM-5, were inactive for DME carbonylation to MA.

The reaction mechanism of DME carbonylation over HEU-12 zeolite was also studied using in-situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. As indicated by Fig. S6 and S7 in ESI†, the adsorption of single DME is on the Brønsted acid sites for methoxyl group formation, and the adsorption of pure CO is on the Lewis acid sites of HEU-12.[14] The in-situ DRIFT analysis on DME carbonylation was performed at varied reaction temperatures 220, 230 and 240 °C (Fig. 3a and Fig. S8-9, ESI†). Higher reaction temperatures will facilitate the activation of DME and CO on the zeolite to form intermediates of acetyl groups (1650 cm^{-1}). But the formation of CO_2 by-product was also promoted because of the emergence of broad peaks (2349 cm^{-1}) at higher reaction temperature of 240 °C. It seems that the DME carbonylation over HEU-12 zeolite obeys the mechanism of methoxyl groups on Brønsted acidic sites interacting with the activated CO by Lewis acidic sites to generate the intermediate of acetyl groups. Based on the mechanism analysis, a possible reaction network for DME carbonylation to MA on HEU-12 was proposed, as shown in Fig. 3b.

For DME carbonylation, the derived hydrocarbons from the decomposition of reaction intermediates would inevitably deposit in the zeolite pores and channels, which therefore block the 8-MR channels and cover the active sites. As a result, the diffusion of the reactants products will be limited severely, thus leading to the catalyst deactivation. In order to investigate the catalytic

Fig.3 (a) In situ DRIFT spectra over HEU-12 zeolite after exposure to DME/CO/Ar for (a) 2 min, (b) 5 min and (c) 10 min at 220 °C; (b) Reaction Scheme of DME carbonylation to MA over HEU-12 zeolite.

deactivation mechanism of HEU-12 zeolite in DME carbonylation, the amount and location of the deposited coke in the spent HEU-12 zeolite after reaction 50 h was further characterized, as given in Fig. 4. The coke content in the spent HEU-12 zeolite was detected using TG analysis. The mass loss of the spent zeolite corresponding to coke combustion was illustrated in Fig. 4b. The TG curve of the spent HEU-12 zeolite can be divided into three major stages according to varied temperatures. The weight loss from 200 to 800 °C was used to obtain the total amount of the formed coke on the spent zeolite. The weight loss at low temperature (200-600 °C) was mainly ascribed to the combustion of the soft coke, i.e., surface-bond methyl and acetyls associated with the formation of MA. And the weight loss between 600 and 900 °C was corresponded to the oxidation combustion of heavy coke, which might be assigned to large hydrocarbons.[12] Possibly, the deactivation behaviour was determined by the quantity of the hard coke in the channels of zeolite, instead of the soft coke on the external surface. The distribution and the amounts of the formed coke on the spent HEU-12 zeolite were determined by N_2 adsorption measurements (Fig. S10 and Table S1, ESI†). For the spent HEU-12 zeolite, there is no clear decrease for its micropore volume, and only a slight reduction for its surface area was observed. The calculation methods of internal and external coke content were similar to the literatures.[13] Based on the analysis results of the TG and BET, we found that the deposited coke formed mainly on the external surface of zeolite during the carbonylation reaction. The internal zeolite pores and channels were not affected at all. The coke deposition mechanism on this HEU-12 zeolite is completely different with the known other zeolite catalysts. The coke formation on the existed zeolites (like MOR and ZSM-35) in carbonylation reaction happened usually inside the zeolite pores and channels, resulting in their quick deactivation. Therefore, the specific coke formation mechanism of HEU-12 was fairly favourable to its excellent stability. To further analyze the cause of deactivation, coke species over the spent zeolite was identified by GC-MS (Fig. S11, ESI†). The coke extracted from the spent HEU-12 consisted mainly of single-ring aromatics with two or more aliphatics branches. Besides, traces of compounds with two-ring aromatics were also identified. Based on the above results, a deduced model of coke formation on HEU-12 during DME carbonylation reaction was proposed (Scheme S1, ESI†).

In order to investigate the potential commercial application of EU-12, the spent catalyst after 50 h reaction was regenerated. XRD patterns displayed that the crystallinity of regenerated HEU-12 catalyst was retained well. The NH$_3$-TPD analysis of the regenerated HEU-12 catalyst revealed that the total acid amount can be recovered to the comparative level as that of fresh zeolite (Fig. S12a, ESI†). It can be seen that the catalytic activity of spent HEU-12 were recovered after the first and second regenerations. The MA selectivity of regenerated HEU-12 catalyst was almost same to that of fresh HEU-12 zeolite (Fig. S12b, ESI†). Furthermore, based on the proposed reaction mechanism, the catalytic activity and MA selectivity over HEU-12 could be improved facilely by decrease the diffusion path or tune the amount of Brønsted and Lewis acid sites with metals.[15] A Cu/EU-12 (Cu: 0.8 wt%, measured by XRF) sample prepared
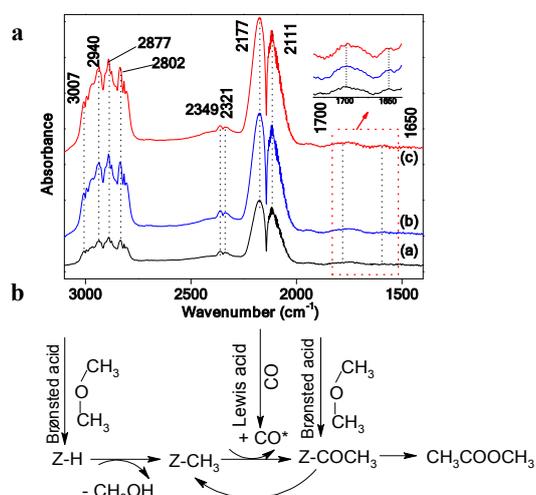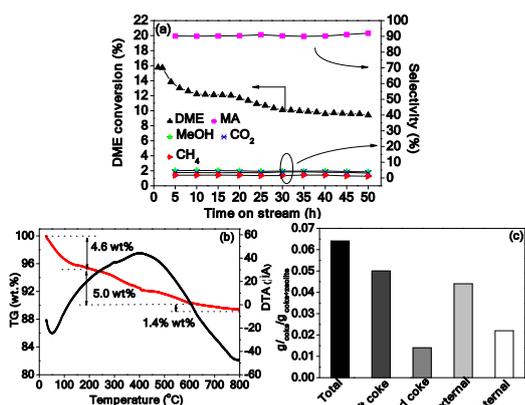
Fig. 4 (a) The catalytic performance of DME carbonylation on HEU-12 zeolite at 220 °C and 1.5 MPa for 50 h; (b) TG-DTA curves of the spent HEU-12 zeolite; (c) the species and distribution of the deposited coke in spent HEU-12 zeolite. Total coke weight was determined by TG analysis, assuming that the weight loss above 200 °C of the spent HEU-12 zeolite is entirely due to coke combustion; reaction condition: feed gas: 3.03% Ar/4.13% DME/ 92.84% CO; flow rate= 20 mL/min, weight $_{(zeolite)}$ =0.5 g.

by ion-exchange method exhibited improved DME conversion and MA selectivity (Fig. S13, ESI†).

In summary, we discovered a brand new zeolite of EU-12 that possesses excellent ability, never been reported before, for carbonylation reaction. The EU-12 demonstrated excellent catalytic stability and selectivity for DME carbonylation to form MA. The conversion of DME slightly decreased form 15.7% at 2 h to 10.0% at 30 h and then became stable at 220 °C. Moreover, the selectivity of MA was kept above 90% during the total reaction process. The discovered EU-12 zeolite for DME carbonylation reaction is very promising and can be also extended to other carbonylation reactions, by which to broaden the application of heterogeneous solid catalyst for the green synthesis of organic chemicals. This finding will also inspire the development of other new zeolite candidates for more efficient carbonylation reaction.

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EU-12 zeolite was discovered to possess unreported catalytic performance for carbonylation reaction converting dimethyl ether to methyl acetate.

DME

EU-12

MA
Sel. ＞90%