



Effect of SSIE structure of Cu-exchanged β and Y on the selectivity for synthesis of diethyl carbonate by oxidative carbonylation of ethanol: A comparative investigation

Pingbo Zhang, Shouying Huang, Yang Yang, Qingsen Meng, Shengping Wang, Xinbin Ma*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Weijin Road 92, Nankai District, Tianjin 300072, PR China

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ABSTRACT

Cu-exchanged β and Y catalysts were investigated by oxidative carbonylation of ethanol in the gas-phase reaction. Cu β catalyst has shown better catalytic selectivity for oxidative carbonylation of ethanol to diethyl carbonate (DEC), without the principal by-product 1,1-diethoxyethane (DEE) for CuY catalysts. In order to investigate the effect of zeolite structure on the selectivity for products, computational analysis of molecular dimensions and diffusion parameters of DEC and DEE within Cu β and CuY catalysts zeolite framework has been performed using molecular mechanics and quantum mechanics methods. The computational analysis results are in good agreement with the experimental results to some extent. DEC having a kinetic diameter of 3.663 Å and the lowest energy barrier was formed preferentially over both zeolites. However, the DEE molecule was not detected among the products over Cu β because of its greater kinetic diameter 6.059 Å and higher energy barrier. The special architecture of β zeolite did not allow the diffusion of DEE molecules through its pores. The formation of the higher sterically hindered DEE over CuY catalyst could be explained by involvement of the outer surface.

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1. Introduction

Diethyl carbonate (DEC) is recognized as an environmentally benign chemical because of its negligible ecotoxicity and low bioaccumulation and persistence. Because of its high oxygen contents (40.6 wt.%), DEC has been proposed as a replacement for *tert*-butyl ether (MTBE) as an attractive oxygen-containing fuel additive [1]. A further significant advantage of DEC over other fuel oxygenates such as MTBE is that DEC could slowly decompose to CO₂ and ethanol, which have little environmental impact when released into the environment [2]. In addition, the gasoline/water distribution coefficients for DEC are more favorable than those for dimethyl carbonate (DMC) and ethanol [3]. Besides these applications as a fuel additive, DEC is also drawing attention as a safe solvent and an additive in lithium cell electrolyte [3–5].

There are several synthetic methods for producing DEC, such as a phosgene process [6], carbonylation of ethyl nitrite [7], oxidative carbonylation of ethanol [8–12], and an ester exchange process [13,14]. Among them, the vapor phase oxidative carbonylation of ethanol represents one of the proposed favorable processes based on the “green chemistry” principles. Previous results have shown

that all of the catalysts prepared by impregnating methods deactivated quickly because of losing the chlorine anion and the remodel of active copper species on the surface [10,15,16]. Recently, Cu-exchanged zeolites have shown to be preferable active catalysts for the oxidative carbonylation of methanol to dimethyl carbonate [17–19]. However, the selectivity for the Cu-exchanged zeolites catalysts was not favorable with the principal by-products being dimethoxymethane (DMM) and methyl formate (MF) [20–22]. Up to now, the influences of zeolite pore structure on the activity and selectivity for DEC synthesis of Cu-exchanged zeolites have not been investigated.

Computational modelling has been shown an efficient method of screening possible catalysts for shape-selective reactions [23]. Catalytic conversion and selectivity of molecules in zeolites were influenced by several factors, molecular dimensions, the pore structure, diffusion energy, etc. Among those factors, the diffusion energy of products could play an important role. The information about interactions at the molecular level is difficult to obtain experimentally. So computer simulation, using molecular dynamics techniques, is an attractive alternative to study the influences of zeolite pore structure on the activity and selectivity for products.

The main objective of this work was to gain the calculation and comparison of diffusional energies for possible products by oxidative carbonylation of ethanol inside the channels of β

* Corresponding author. Tel.: +86 22 27406498; fax: +86 22 27890905.
E-mail addresses: xbma@tju.edu.cn, xinbinma@gmail.com (X. Ma).

and Y zeolites. In the present work, the catalytic performances of Cu-exchange β and Y catalysts by oxidative carbonylation of ethanol in the gas-phase reaction were investigated. The experimental results were compared with the computer simulation results to find an explanation at the molecule level for different behaviours of products in these zeolites in the studied reactions.

2. Experimental and methods of calculation

2.1. Experimental

The catalysts were prepared by solid-state ion exchange (SSIE) of the protonated form of each zeolite (Y: Si/Al = 5; β : Si/Al = 20) with CuCl in a flow of N_2 at a heating rate of $10^\circ C/min$ up to the desired temperature $550^\circ C$ and then held for 6 h.

2.2. Production and analysis of product

Catalytic activity was measured by a computer-controlled continuous microreactor system (WFS-3015) with a quartz tubular reactor of 4 mm inner diameter. The reaction products collected in the cooling trap were taken out and sampled every hour, and were analyzed by a gas chromatograph (GC) (4890D, Agilent) with a FID detector. The uncondensed gas products were introduced to the gas chromatograph (GC-8A, Shimadzu) through an on-line six-way valve and analyzed by a TCD detector with a TDX-01 and Propak-Q packed column. The reaction conditions were steadily kept at a reaction temperature of $140^\circ C$ and a reaction pressure of 0.64 MPa.

2.3. Methods of calculation

The Material Studio (Version 3.1) software package was used for computational modelling analysis. The analysis was based on energies, dimensions and diffusion energies of the molecules in the zeolite. The molecular dimensions of studied molecules DEC and DEE were calculated using the *Dmol³* module function of Material Studio 3.1. The diffusion energies of the molecules inside zeolite channel were computed using the *Discover* module of Material Studio 3.1. The FAU (Y zeolite) and BEA (β zeolite) channels structure were from *zeolite* in Material Studio 3.1 and optimized with SiO clusters ($Si_{196}O_{384}Al_{96}$ for a FAU cluster and $Si_{256}O_{512}$ for a BEA cluster). It must be pointed out that, for these calculations, an ideal channel of the zeolite is used. Additional factors, such as the chemical composition of the zeolite framework and the acidic properties of the zeolite together with the mechanism of the formation of the products (primary or secondary) were not taken into account.

Molecular diffusion energies calculations were used by CVFF force field [24]. During the calculation of diffusion energies, the product molecules moved from jumping-off point to end point in the paths, which were chosen in advance. The product molecule

was forced to diffuse stepwise, in steps of 0.1 \AA inside the 12 m channel between two points, which defined the diffusion path. These two points were located at the mid-points of the pore apertures of the 12 m channel in zeolites β and Y. In every position, the minimized diffusion energies were searched. The diffusion energies (E_{dif}) were calculated by the following expression:

$$E_{dif} = E_{z-d} - (E_z + E_d)$$

In the expression, E_{dif} is the molecular diffusion energy in zeolite, E_{z-d} denotes the system energy of zeolite and diffusing molecule, E_z is the energy of only zeolite and E_d shows the energy of only molecule.

3. Results and discussion

3.1. Catalytic results of Cu-exchange β and Y catalysts

The catalytic results of Cu-exchange β and Y catalysts on oxidative carbonylation of ethanol with CO and O_2 were shown in Table 1. The distribution of products for Cu-exchange β and Y catalysts system was completely different in Table 1. The Cu β catalysts showed better selectivity to DEC based on ethanol without DEE formation. Although CuY catalysts exhibited similar conversion of EtOH, the selectivity for DEC was not favorable. Consequently, the Cu β catalysts attracted much attention because of its relative higher yield of DEC. In addition, substantial amounts of the by-products, ethyl acetate and acetaldehyde, were produced under CuY catalysts system, while the by-products for Cu β catalysts only contained acetaldehyde.

As known, distribution of products over zeolite catalysts was influenced by several factors, products' shape, size and the diffusion energy, etc. Hence, molecular dimensions and diffusion energy of studied molecules were calculated in succession.

3.2. Molecular dimensions

The molecular representations of DEC and DEE were shown in Fig. 1. The smallest sectional (or critical) diameters of DEC and DEE were calculated using the *Dmol³* module function of Material Studio 3.1. From Fig. 1, the DEE molecule is approximately like cage

Table 1
Comparison of Cu-exchange β and Y catalysts systems on catalytic performance.

Catalyst	Conversion of EtOH (%)	Selectivity (%)			
		DEC	DEE	Ethyl acetate	Acetaldehyde
Cu β	4.3	78.4	0	0	21.6
CuY	4.2	23.9	56.1	10.9	9.1

Reaction condition: $T = 140^\circ C$, $P = 0.64 \text{ MPa}$, $O_2 = 4 \text{ sccm}$, $CO = 40 \text{ sccm}$, $N_2 = 26 \text{ sccm}$.

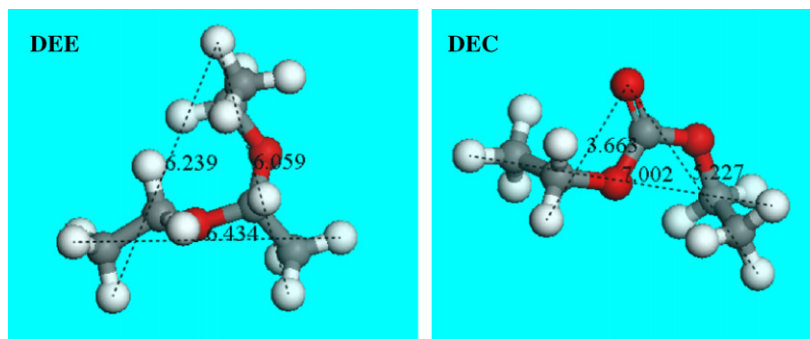


Fig. 1. Molecular representations of 1,1-diethoxyethane (DEE) and diethyl carbonate (DEC).

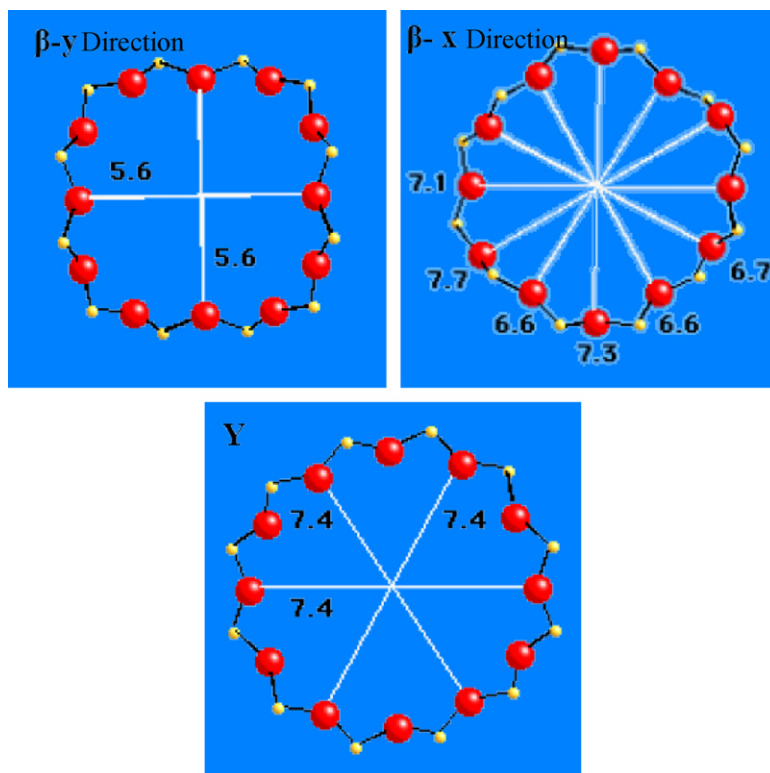


Fig. 2. The pore structure of β and Y zeolites.

type and the smallest sectional diameter of DEE is 6.059 Å. And the DEC molecule approximates fold line type and the smallest sectional diameter of DEC is 3.663 Å.

The pore structures of β and Y zeolites are different, as shown in Fig. 2. β zeolite has a three-dimensional interconnected (3D) channel system with 12-membered ring openings. Interconnected linear pores with an opening of $7.6 \text{ \AA} \times 6.6 \text{ \AA}$ run in X direction, and communicate through perpendicular connecting openings of $5.6 \text{ \AA} \times 6.6 \text{ \AA}$ in the Y direction [25,26]. Y zeolite also has a three-dimensional interconnected (3D) channel system with only one 12-membered ring openings of $7.4 \text{ \AA} \times 7.4 \text{ \AA}$.

From molecular dimensions and pore structure of zeolites, DEC molecule of fold line type easily diffused through both channels of β and Y zeolites. Whereas the smallest sectional diameter of DEE molecule like cage type was larger than pore dimension of β zeolite from Y direction. So DEE molecule hardly diffused through both channels of β zeolite from Y direction. From Table 1 in the reaction over Cu β zeolite, DEC was observed as the main product with relatively small amounts of acetaldehyde. This may be attributed to the different architecture of pores ($7.7 \text{ \AA} \times 6.6 \text{ \AA}$, $5.6 \text{ \AA} \times 5.6 \text{ \AA}$ interconnected channels, absence of supercages in β) in which DEE cannot freely move. The results clearly indicated that the pore architecture and pore dimensions of β zeolite were suitable for the selective synthesis of DEC.

Hereinbefore, effect of selectivity of products over β and Y zeolites was investigated from molecular dimensions and pore structure of zeolites. The results observed on the basis of molecular dimensions and pore structures of zeolites predicted that β zeolite could be a potential catalyst for shape-selective oxidative carbonylation of ethanol. In fact, molecules may arise from a possible conformational flexibility during diffusing in the channels of zeolites. And the preferential formation of DEE against DEC on Y zeolites possibly arises from their differences in diffusion kinetics although the two molecules could easily diffuse in enough empty space with small molecular diameters. The

calculation of diffusion energies of the molecules inside zeolite channel is necessary.

3.3. Diffusion energies

The channels dimensions from X direction of β zeolite are different from those from Y direction. So energy parameters on the basis of both diffusion channels were calculated over β zeolite. The diffusions of the molecule of DEC in β and Y zeolite were taken graphic example in Figs. 3–5. Energy profile for the diffusion of DEC in β zeolite from X direction was taken example for the calculation

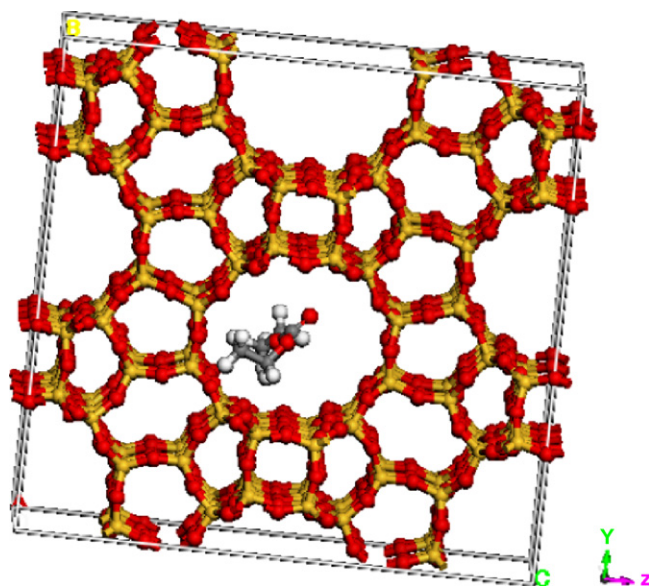


Fig. 3. Molecular representation of DEC in channel of β zeolite from X direction.

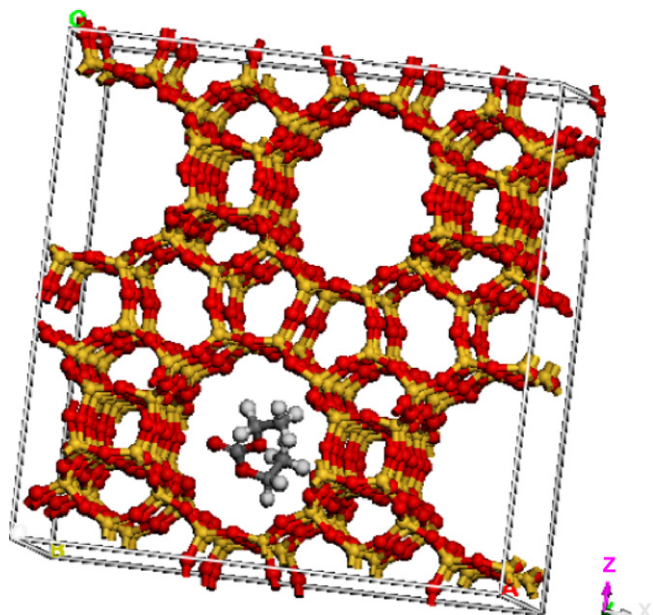


Fig. 4. Molecular representation of DEC in channel of β zeolite from Y direction.

of diffusion energies in Fig. 6. The diffusion energy profiles of other products in zeolites were not particularized one by one.

The energy parameters calculated from the diffusion energy profiles for DEC and DEE in β and Y zeolites channel were listed in Table 2. Although there was more empty space available in channel of Y than in β , the energy barrier values calculated for DEC and DEE in channels of Y zeolite were higher than those obtained for β zeolite in Table 2. DEC had a lower energy barrier in comparison with DEE in β zeolite channel from X and Y directions, which supported the products distribution in experimental results from Table 1. It was found that DEC had the lowest energy barrier (–38.91 kcal/mol) in β zeolites channel from Y direction among products. This computational analysis of diffusion energy for DEC in β zeolites channel was in good agreement with the yield of DEC over Cu β catalyst. Although DEE had low diffusion energy barrier in β zeolites channel from X and Y direction, DEE was absent among the products over Cu β catalyst. It could be interpreted by

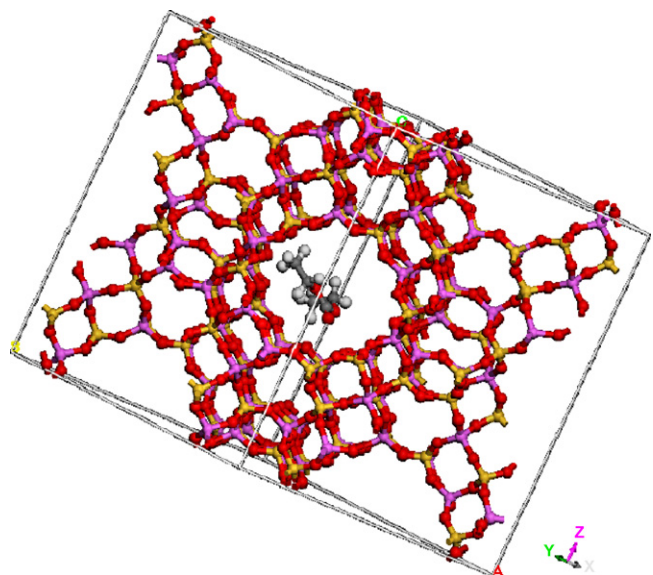


Fig. 5. Molecular representation of DEC in channel of Y zeolite.



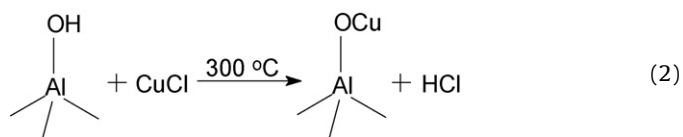
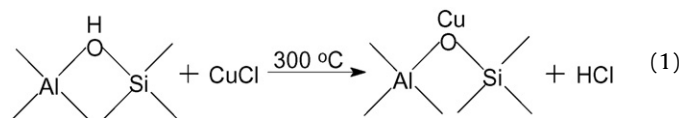
Fig. 6. Energy profile for the diffusion of DEC in β zeolite from X direction.

the special architecture of β zeolites and smallest sectional diameter of DEE.

As known, the active center of Cu-exchanged zeolites catalysts is formed by the reaction that Cu⁺ atom of CuCl replaced the H⁺ of the OH group in the zeolite with the releasing of HCl. Most Brønsted acidic sites were presented in the inner surface of pore channel of β zeolite [27]. The active centers of Cu-exchanged zeolite catalysts were formed by the interaction of gaseous CuCl and H⁺ of Brønsted acidic sites in the zeolite. Therefore, most active center of Cu β catalyst located in the inner surface of pore channel of β zeolite, and there existed almost no active center in the outer surface. From this point, the reason why DEE is not produced on the outer surface of Cu β was easily understood.

And in case of Y zeolites, the higher sterically hindered DEE over CuY catalyst had the higher yield among the products, which was somewhat different from the experimental results.

Spoto et al. have studied in detail the state of copper in copper-zeolite materials made by interactions of H-form zeolite with gaseous CuCl [28]. They discovered that gaseous CuCl reacts with H⁺ of the most acidic Brønsted sites of the zeolite at 300 °C as the following schemes, which were connected with the Al atom. It was difficult to react with only H⁺ from the HO–Si–. Therefore, the more Al content in the zeolites facilitates the more catalyst active centers forming, and the more active centers maybe advanced the performance of the catalysts.



In CuY catalyst system, the content of Al was much more than that of Cu β because Si/Al (5) ratio of CuY was lower than that of Cu β

Table 2
Diffusion energies of products in channel of β and Y zeolites.

Product molecule	$E_{\text{dir}}(\beta\text{-X})$ (kcal/mol)	$E_{\text{dir}}(\beta\text{-Y})$ (kcal/mol)	$E_{\text{dir}}(\text{Y})$ (kcal/mol)
DEC	–38.61	–38.91	–32.81
DEE	–34.81	–33.91	–26.71

(20). So there were a mass of active centers of Y zeolite, which existed not only in the inner surface of pore channel but also on the outer surface of the frame [29]. Therefore, the formation of DEE over CuY catalyst could be explained rightly by involvement of the more active centers on the outer surface, which was not influenced by the pore structure of zeolite and molecule diffusion in the channel. Hence, the results of computational analysis for sterically hindered DEE over CuY catalyst are reasonable considered from this point.

4. Conclusion

Cu-exchanged β and Y catalysts showed different selectivity to DEC by oxidative carbonylation of ethanol in the gas-phase reaction. Cu β catalyst has been shown better catalytic selectivity for oxidative carbonylation of ethanol to DEC, without the principal by-product 1,1-diethoxyethane (DEE) for CuY catalyst. Cu β catalyst was predicted to be a shape-selective catalyst for synthesis of DEC by oxidative carbonylation of ethanol.

The calculated values have been compared with the experimental results obtained in the oxidative carbonylation reaction of ethanol over Cu-exchanged zeolites catalysts. In the case of the reaction, the computational analysis results were in good agreement with the experimental results achieved in the oxidative carbonylation reaction of ethanol over Cu β and CuY zeolites catalysts on the whole. The kinetic diameter of DEC is 3.663 Å and the lowest energy barrier was obtained for DEC in β channel from Y direction. So DEC was formed preferentially over Cu β catalyst. While the more hindered DEE having greater kinetic diameters 6.059 Å was formed over CuY catalyst. The special architecture of β zeolite was the main reason that it did not allow the diffusion of relatively hindered DEE molecules through its pores. Therefore the main by-product diethoxyethane (DEE) for CuY catalysts was not detected in the oxidative carbonylation reaction over Cu β catalyst.

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