

Density functional theory study of side-chain alkylation of toluene with formaldehyde over alkali-exchanged zeolite



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ABSTRACT

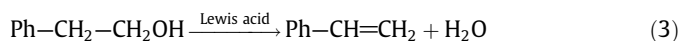
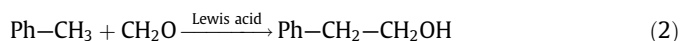
The adsorption of the alkali-metal cation ($M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$) and the reaction mechanism of the side-chain alkylation of toluene with formaldehyde over MY basic zeolite ($M = \text{Rb}^+$ and Cs^+) were investigated using density functional theory calculations. During co-adsorption, the zeolite adsorbs toluene preferentially and then formaldehyde. The side-chain alkylation in MY zeolite ($M = \text{Rb}^+$ and Cs^+) consists of the following two steps: toluene reacts with formaldehyde to obtain phenyl ethanol, and then the intramolecular dehydration of phenyl ethanol produces styrene and water. Phenethyl alcohol dehydroxylation is the rate-controlling step. Although the activation energy is similar in Rb^+ - and Cs^+ -modified zeolite (63.09 and 62.20 kcal mol⁻¹), the products are much easily removed from the system in Cs^+ -modified zeolite. Scilicet, Cs^+ -modified zeolite is a suitable catalyst during the side-chain alkylation of toluene.

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1. Introduction

Styrene is an important industrial chemical used to synthesize and manufacture polystyrene and copolymers, as well as numerous other industrial resins. The conventional method of styrene production, which accounts for >90% of the total world styrene production, involves two subsequent reactions: the alkylation of benzene with ethylene to produce ethylbenzene and the dehydrogenation of ethylbenzene to styrene. In 1967, Sidorenko et al. [1] first reported that alkali-exchanged zeolites catalyze the side-chain alkylation of toluene with methanol to styrene. Since then, this reaction has been the subject of several experimental and theoretical studies [2–10]. The scientific interest on side-chain alkylation of toluene with methanol over alkali-exchanged zeolite increases because the reaction constitutes a more environmentally benign and lower raw-material-cost process compared with traditional Fredel–Crafts alkylation. Despite these efforts, a side-chain alkylation catalyst that produces high conversion and selectivity has not been reported and a consensus has not been reached regarding the mechanism of the reaction [1,2,6,10–15].

The generally accepted mechanism [2,3] for alkylation of styrene with toluene and methanol over a basic zeolite catalyst is as follows:



The first elementary step for side-chain alkylation in basic zeolites is the dehydrogenation of methanol to form formaldehyde. This step has been extensively studied in literature [10,16–18]. Thus, in the present study, we focus on the steps involving co-adsorption of toluene and formaldehyde in the alkali metal cation zeolites and their reaction mechanisms. The detailed reaction mechanism will facilitate the optimization of the reaction condition and the manufacture of better catalysts for the reaction.

2. Computational methods

The experimental results show that the majority of the alkaline earth metal cations are located at site SII (Fig. 1) [19,20]. Small cations ($\text{Li}^+, \text{Na}^+, \text{K}^+$) are completely embedded in the silicate ring, whereas larger cations (Rb^+ and Cs^+) increasingly protrude towards the reaction space. The cluster model that represents the zeolite structure has been extensively used to investigate zeolite-catalyzed reactions [21–30]. In this paper, we used an isolated 6-membered-ring (6MR) cluster to describe the zeolite framework (Fig. 2). The framework of the 6MR model was obtained from site

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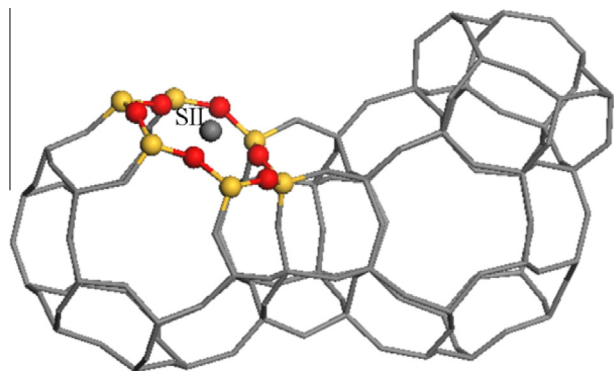


Fig. 1. The 6mr model is taken from the site II of Y zeolite. The gray atom is denoted as alkali-metal atom.

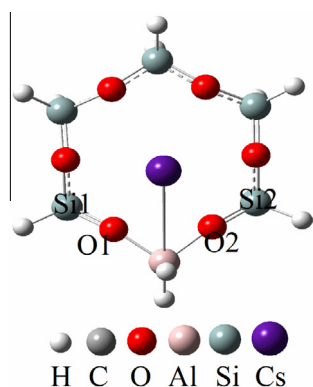


Fig. 2. The top view of the cluster model including a single six-membered ring (6MR) and a cation Cs at site II.

SII of the Y zeolite, wherein dangling Al and Si bonds are saturated by hydrogen atoms.

All density functional calculations were performed using the Gaussian09 program package [31]. No geometric constraints were assumed in the geometry optimization. All structures were optimized and characterized by B3LYP/LANL2DZ (the LANL2DZ basis set for Li, Na, K, Rb, and Cs atoms and 6-31G++** basis set sequentially for Si, Al, O, C, and H atoms). The frequencies of all the geometries were calculated at the same level to identify the nature of the stationary points and obtain the zero-point-energy (ZPE) corrections. All stationary points were characterized as minima (no imaginary frequencies) or transition state (one imaginary frequency) by a Hessian calculation. The intrinsic reaction coordinate (IRC) calculations [32,33] were used to identify that each transition state links the correct product with the reactant. Basis set superposition error (BSSE) corrections evaluated by the counterpoise method [34] were also considered.

DFT methods present the drawback of not properly describing the van der Waals dispersive contribution [35–38]. Therefore a van der Waals energy correction has been applied on the toluene adsorption energy by using the parameters defined by Grimme et al. [39,40] for aromatic species within zeolites. During the process of correction, we used Becke–Johnson damping, which is more explicit in physical meaning and can make the results better [40]. The expression of the computed van der Waals energy contribution is:

$$E_{\text{vdW}}^{\text{DFT-D3(BJ)}} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{R_{AB}^n + f(R_{AB}^0)^n}$$

$$f(R_{AB}^0) = a1R_{AB}^0 + a2$$

where R_{AB} denotes interatomic distance and C_n^{AB} is van der Waals correction coefficient and s_n is calibration factor. Each functional has four parameters, namely, a1, a2, s6, s8. For ordinary functional, the value of s6 is 1, and the other three parameters need fitting to confirm generally.

The van der Waals correction has been applied to all consecutive intermediates and transition states. The corrected van der Waals adsorption energy is expressed as:

$$E_{\text{ads}}^{\text{corrected}} = E_{\text{ads}} + E_{\text{vdW}}^{\text{DFT-D3(BJ)}}$$

where E_{ads} is the adsorption energy obtained by the cluster structure calculation and $E_{\text{vdW}}^{\text{DFT-D3(BJ)}}$ is van der Waals energy correction.

3. Results and discussion

3.1. Co-adsorption of toluene and formaldehyde

We constructed two different co-adsorption types, 6mr-M-T-F and 6mr-M-F-T, to further understand the interaction between formaldehyde and toluene and the effect of the two components on the entire co-adsorption system. 6mr-M-T-F denotes that the zeolite will first adsorb toluene on a cluster (6mr-M-T) then continue to adsorb formaldehyde (F); 6mr-M-F-T denotes that the zeolite will adsorb formaldehyde on a cluster first (6mr-M-F) then continue to adsorb toluene (T). This analysis on the type of co-adsorption has been used in many papers [41–43]. All the optimized structures of the co-adsorption complexes are displayed in Figs. 3 and 4. The geometric data, Mulliken partial charges (au), and adsorption energy (kcal mol⁻¹) of 6mr-M-F-T and 6mr-M-T-F are shown in Tables 1 and 2.

$$E_{\text{ads}} = (E_{6\text{mr-M-F}} + E_{\text{T}}) - E_{6\text{mr-M-F-T}}$$

$$E_{\text{ads}} = (E_{6\text{mr-M-T}} + E_{\text{F}}) - E_{6\text{mr-M-T-F}}$$

We compared 6mr-M-F (Supporting information, Table 2) and 6mr-M-F-T (Table 1). The adsorption energies 11.71–15.83 kcal mol⁻¹ of 6mr-M-F are higher than 6.93–9.39 kcal mol⁻¹ of 6mr-M-F-T. Thus, 6mr-M adsorbs formaldehyde quite easily, followed by a relatively difficult adsorption of toluene. After adsorption of toluene (6mr-M-F-T), no significant change in C=O3 bond lengths and vibration frequency of formaldehyde were observed compared with 6mr-M-F. Thus, formaldehyde is not further activated by the adsorption of toluene. A comparison between 6mr-M-T (Supporting information, Table 3) and 6mr-M-T-F (Table 2) revealed that the adsorption energies of 6mr-M-T-F (11.75–16.38 kcal mol⁻¹) are higher than 6mr-M-T (8.38–12.62 kcal mol⁻¹). Thus, 6mr can still strongly adsorb formaldehyde after relatively weak adsorption of toluene. In addition, we compared the q(C) (negative charge on the methyl carbon atom of toluene) in 6mr-M-T and 6mr-M-T-F. q(C) in 6mr-M-T-F is higher than in 6mr-M-T. Thus, the adsorption of toluene enhances the activity of the methyl carbon atoms, which is conducive to a better alkylation side reaction. Moreover, the adsorption of formaldehyde would first increase the distance between toluene and zeolite, which is not conducive to the activation of the methyl carbon atoms and results in the insignificant breaking of C–H. However, according to the thermodynamics of the reaction medium based on calculated adsorption energies (Supporting information), the adsorption of formaldehyde on a zeolite cluster is much stronger than that for toluene. Actually, we must be aware of that there is no direct relationship between modeling sequence and adsorption sequence.

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