Mechanistic insights into hexane conversion to aromatics over gallium embedded zeolites

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Abstract: The catalytic mechanism of hexane conversion to benzene over Ga embedded H-ZSM-5 zeolites was investigated using density functional theory (DFT) calculations. The reaction mechanism has been proposed via the following two main steps: (i) dehydrogenation of *n*-hexane to haxa-1,3,5-triene; (ii) the aromatization of haxa-1,3,5-triene to benzene. Moreover, the effect of hydrogen pretreatment on structurally Ga active species was also discussed in terms of both experimental and theoretical points of view. Interestingly, the presence of H_2 incorporated on the catalytic Ga-embedded zeolites can greatly promote the reaction and thus makes it kinetically feasible.

Keywords: DFT, Gallium, Zeolite

1. Introduction

The catalytic cracking, oligomerization, dehydrogenation, and aromatization of alkanes to aromatics has been considered in both scientific and industrial points of view because they are important steps for the alkane upgrading to more valuable hydrocarbons, such as benzene, toluene, and xylene (BTX). Zeolites, highly ordered porous aluminosilicate materials, are well-known catalysts for promoting the catalytic cracking of light alkanes and aromatization of hydrocarbons. Moreover, the modification of zeolites by various metals, such as gallium (Ga), zinc (Zn), and tungsten (W) can greatly enhance the catalytic conversion and selectivity for aromatic products and the resistance of catalyst deactivation. Many experimental[1-3] and theoretical[4] observations suggested that the gallium cation (Ga^+) modified H-ZSM-5 zeolite is one of the most promising catalysts for the catalytic conversion of alkanes to aromatics. However, the reaction mechanisms of the alkane aromatization over Ga species in Ga/H-ZSM-5 are debated. To clarify the reaction mechanisms over various gallium species (Ga^+ and GaH_2^+) embedded H-ZSM-5, the quantum chemistry simulations by means of DFT approaches were performed. In this context, we demonstrate insights into the catalytic mechanism of *n*-pentane conversion to benzene as a model reaction over various gallium active sites.

2. Theoretical studies

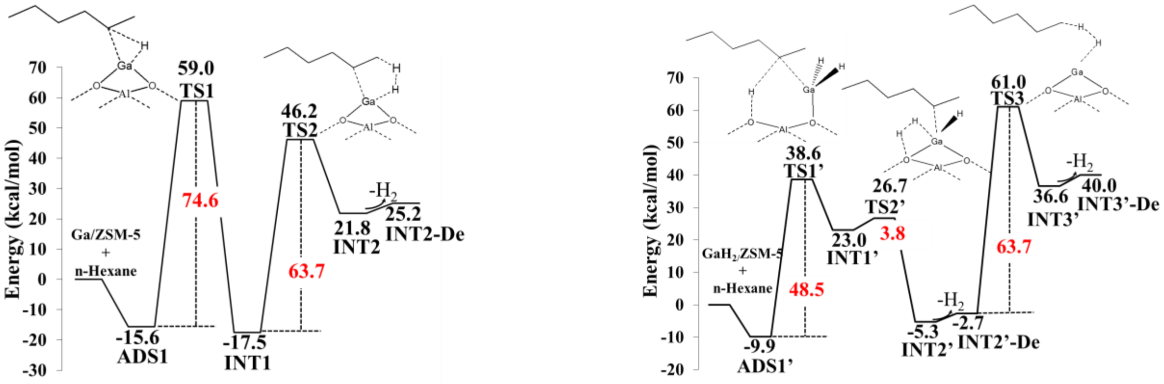
The model of ZSM-5 was represented by the 14T cluster generated from its lattice parameters[4] as shown in Figure 1. Two aluminium atoms substituted to silicon atoms at T9 and T12 sites (Figure 1a). These sites located at two intersecting five-membered rings of the ZSM-5 zeolite straight pore. In the model of gallium cation supported ZSM-5, the Brønsted acid site of zeolite on the oxygen bridging of a five-membered ring was exchanged by the gallium cation (Ga^+) and gallium dihydryl cation (GaH_2^+) (Figure 1). All calculations were performed using GAUSSIAN 09 code with the M06-2X density functional and the basis set of 6-31G(d,p)[5].

a b

Figure 1. Optimized structures of 14T models of a) Ga/H-ZSM-5 and b) GaH_2/H-ZSM-5.

3. Results and discussion

The process of hexane conversion to benzene requires many steps. The key step of the reaction is the dehydroaromatization of *n*-hexane to benzene. The reaction mechanism of this step has been proposed by two main steps: (i) dehydrogenation of *n*-hexane to haxa-1,3,5-triene; (ii) the aromatization of haxa-1,3,5-triene to benzene. The first step of the *n*-hexane dehydrogenation to hexa-1-ene over Ga/H-ZSM-5 is considered to be the rate determining step and requires a high activation energy of 74.6 kcal/mol proceeded via TS1 as the transition state (Fig. 2a, TS1). Obviously, the rate determining step is the second step of *n*-hexane dehydrogenation to hexa-1-ene via TS3 with a significantly lower barrier energy of 11 kcal/mol (Fig. 2b, TS3) over GaH_2/H-ZSM-5. For the aromatization step of haxa-1,3,5-triene to benzene, this step requires a low activation energy of 27.3 kcal/mol for both active species. The results indicate that the H_2 incorporated on Ga embedded zeolite, which generated by H_2 pretreatment can promote the catalytic activity of the reaction.



a b

Figure 2. Energy profile of *n*-hexane dehydrogenation to hexa-1-ene over a) Ga/ZSM-5 and b) GaH_2/ZSM-5.

4. Conclusions

The reaction mechanism of hexane conversion to benzene on Ga/ZSM-5, and GaH_2/H-ZSM-5 formed by the H_2 molecule introducing has been calculated by using M06-2X density functional. The dehydrogenation step of *n*-hexane dehydroaromatization is considered as the rate determining step. For the Ga/H-ZSM-5, the *n*-hexane hydrogen abstraction over Ga/H-ZSM-5 is found to be the rate-determining step with the activation energy of 74.6 kcal/mol. In the case of GaH_2/H-ZSM-5, the rate limiting step relates to the *n*-hexane dehydrogenation to hexa-1-ene with the activation energy of 63.7 kcal/mol. The activation energy is 10.9 kcal/mol lower than that of the corresponding Ga/H-ZSM-5. It clearly demonstrates that the reaction of the hexane dehydroaromatization to benzene is kinetically favored on the GaH_2/H-ZSM-5 zeolite.

References

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