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Interaction of Zn^{2+} with extraframework aluminum in HBEA zeolite and its role in enhancing *n*-pentane isomerization

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ABSTRACT

The electrodeposition method was used to produce Zn^{2+} cation precursors, followed by the introduction of Zn^{2+} cation precursors to HBEA by the ion exchange technique. The introduction of Zn^{2+} cations slightly changed the specific surface area and crystallinity of HBEA. IR, XPS and solid state MAS NMR results showed that Zn^{2+} cations interacted with $(AlO)^+$ extraframework aluminum to form $Zn(OAl{=})_2$ and simultaneously induced the formation of bridging hydroxyl groups, Si(OH)Al. The pyridine adsorbed IR study revealed that the presence of Zn^{2+} cations fully eliminated weak and partially eliminated strong Brønsted acid sites. As a result, strong and relatively weak Lewis acid sites were formed in which the pyridine probe molecule desorbed at 623 K and below. The presence of Zn^{2+} cations enhanced the catalytic activity of HBEA in *n*-pentane isomerization due to the presence of strong Lewis acid sites; the sites may facilitate the formation and maintenance of active protonic acid sites through a hydrogen spillover mechanism. At 598 K, the yield of isopentane for Zn-HBEA was 25.7% higher than that of HBEA. Within a reaction temperature range of 373–648 K, the apparent activation energy for isomerization of *n*-pentane over HBEA and Zn-HBEA was 118.76 and 90.79 kJ/mol, respectively.

1. Introduction

Hydroisomerization of paraffins to enhance the octane number of gasoline is an environmentally more acceptable method compared to other technologies such as blending with oxygenates like MTBE, which has been identified as a source of groundwater contamination. It is clear that branched paraffins are the preferred gasoline component; therefore, it is highly desirable to increase the contribution of high octane branched paraffins to the gasoline pool [1]. Alkane isomerization is typically carried out over bifunctional metal-acid catalysts [2] and it is well established that the isomerization proceeds through consecutive branching reactions. Isomerization takes place at the acid sites of the bifunctional catalyst, whereas the metal site provides hydrogenation–dehydrogenation capability. Several types of solid acid catalyst such as MOR [3], SAPO-11 [4], ZSM-22 [5], ZSM-5 [6,7], Beta [8,9], HY [10,11] and oxoanions loaded on ZrO_2 [2,12–14] have been used for the isomerization process. The addition of noble or transition metals to catalysts and the presence of hydrogen in the gas phase markedly improve the activity and stability of the catalyst. Transition metals such as platinum, zinc and iridium cations loaded on support catalysts have also been reported to improve the production of isoproducts and to suppress the cracking reaction in *n*-heptane isomerization over Pt/HY zeolite [7,15,16]. These cationic transition metals might play an important role in speeding up the desorption of olefinic species from the surface of the catalyst, thereby preventing the secondary reaction and/or thermal decomposition of reactants and products.

Particularly, the roles of Zn metal in solid catalysts have been discussed by several research groups in recent years. Saberi et al. reported on *n*-heptane isomerization over Pt–Zn–HY trifunctional catalysts in which they concluded that each reaction temperature needs a specific Zn loading in order to obtain the maximum activity for isomerization [9]. Freude and co-workers explored the properties of Zn/H–BEA zeolite by ^1H MAS NMR and IR spectroscopy of adsorbed CO [17,18]. Kazansky et al. reported that Zn^{2+} ions introduced into ZSM-5 zeolites resulted in the partial localization of Zn^{2+} ions at negatively charged tetrahedral $AlO_4{}^-$, which led to a partial decrease in the Brønsted acidic sites and obstruction of the remaining bridging OH groups [19]. This factor led to a considerable suppression of the cracking activity of zeolites which certainly needs proton donor centers. An extension of the study

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