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Isomerization of *endo*-dicyclopentadiene using Al-grafted MCM-41

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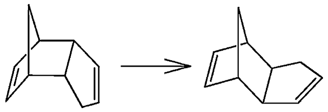
ABSTRACT

The isomerization of *endo*-dicyclopentadiene (*endo*-DCPD) using Al-grafted MCM-41 was studied as an industrial practical synthesis route for *exo*-DCPD. The catalyst was prepared with post-synthesis grafting method, characterized by XRD, N_2 adsorption/desorption, ^{27}Al and ^{29}Si MAS NMR, *in-situ* pyridine adsorption IR and NH_3-TPD. The materials retain ordered mesoporous structure and high surface area. Al atoms are preferentially anchored in tetra-coordination, but these in octa-coordination increase significantly in case of high Al content. The amount of Brønsted acid is closely related to the amount of tetra-coordinated Al species whereas that of Lewis acid corresponding to the total Al content. The prepared material shows higher activity than microporous zeolites because its mesoporous structure gives free diffusion and excellent coke tolerance capability. A good correlation between the conversion of *endo*-DCPD and the amount of Lewis acid was observed. Specifically, the weak Lewis acid sites catalyze the *endo*- to *exo*-isomerization, meanwhile the moderate ones account for the [2 + 2] cycloaddition of two DCDP molecules. Catalyst with Si/Al of 8 is most active due to its highest concentration of weak Lewis acid. Addition of inert solvent, relatively low reaction temperature and high catalyst dosage can improve the isomerization. The deactivated catalyst can be easily regenerated by calcination.

1. Introduction

Dicyclopentadiene (DCPD), a component derived from C_5 fraction of naphtha pyrolysis and coal tar, is an important intermediate or monomer for polymers, rubbers, reaction injection modeling materials and high energy fuels [1–6]. DCPD has two stereoisomers, namely *endo*- and *exo*-isomers, and the latter is preferred in many applications. *exo*-DCPD possesses better fluidity under room temperature and is easy to handle with, and the polymers produced with it show higher melting point and rigidity [1,2]. Specifically, *exo*-DCPD is very attractive in synthesizing high energy jet fuel. For example, hydrogenated *exo*-DCPD (*exo*-THDCPD) is the major component of a jet fuel named JP-10 [3–6]. Unfortunately, naturally obtained DCPD is in form of *endo*-configuration.

There is already a two-step method for the preparation of *exo*-DCPD from *endo*-DCPD, in which HI or HBr is added to the double bond in the norbornene unit of *endo*-DCPD and then eliminated by alcoholic potassium hydroxide, accompanied with the configuration transfer [7,8]. A similar catalytic hydration–dehydration process was also claimed in patent [9]. Recently, we have investigated the one-step isomerization of *endo*-DCPD (see Eq. (1)) [10,11]. Specifically, microporous zeolites like Hβ were found to be active for this reaction. This finding would open a new way to synthesize *exo*-DCDP based on heterogenous catalysis. However, the efficiency is still low due to serious coke formation over strong acid sites and blockage of micropores [10].


endo-DCPD *exo*-DCPD (1)

MCM-41 has attracted great attention in the field of catalysis due to its uniform hexagonal mesoporous structure and high surface area [12,13]. The pore size of MCM-41 ranges from 1 to 10 nm according to different synthesis methods [14,15], which is suitable for the transformation of large molecules like DCPD. Also, the mesoporous structure may provide good coke tolerance. It is expected that MCM-41 would be favorable for the isomerization of *endo*-DCPD. However, the acid concentration of silica MCM-41 is extremely low, which limits its application as acid catalyst. Incorporation of heteroatoms such as Al into the siliceous framework is an efficient way to generate acid sites, and these materials have been reported as good catalyst for many reactions [15–21]. There are generally two methods to prepare Al-contained MCM-41, *i.e.* direct- and post-synthesis. The post-synthesis alumination generates aluminosilicate materials with readily accessible acid sites on the inner walls of mesoporous framework and offers advantages over direct-synthesis with respect to structural ordering and stability [22]. In addition, it is reported that the acidity of Al-MCM-41

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