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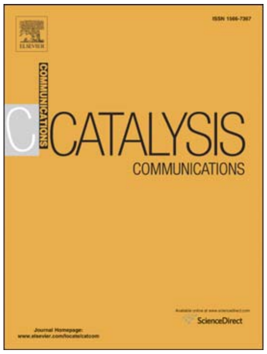

Catalytic performance of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) in the isomerization of Endo- to exo-dicyclopentadiene

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Catalytic Performance of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) in the Isomerization of endo- to exo-Dicyclopentadiene

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ABSTRACT

MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr), metal-organic frameworks (MOFs), have been assessed in solvent-free isomerization of dicyclopentadiene (DCPD) from the endo- to exo-form. In the isomerization reaction, the conversion of endo-DCPD and selectivity for the exo-dimer strongly depend on the nature of the active metal center. The MIL-100 (Fe) catalyst possessing more acid sites shows the highest catalytic activity among the MILs and it was readily recoverable and reusable in subsequent reaction cycles for the isomerization. The effects of reaction parameters such as temperature, reaction time, and catalyst loading on the reactivity were also investigated.

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Keywords: MOF, Isomerization, Dicyclopentadiene, Solvent-free, Acidic catalysis

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1. Introduction

Metal-organic frameworks (MOFs) constitute an emerging class of hybrid inorganic-organic porous materials, which have attracted considerable attention owing to a unique combination of properties, such as crystalline open structures, extremely high surface areas and pore volumes, and regular and accessible pores and functionality [1]. These porous materials are promising for potential applications in gas storage, separation, and heterogeneous catalysis [2], [3] and [4]. Most MOFs potentially combine advantages of both homo- and heterogeneous catalysts because their structures consist of isolated metal clusters or atoms connected by polydentate organic ligands to form a rigid porous framework [5]. The presence of coordinatively unsaturated metal sites (CUS) in some of these MOFs enables their interactions with substrates, the metal ion or cluster acting as a Lewis acid or redox center [6] and [7].

MIL-100 (Fe) demonstrated catalytic activity in the oxidations of diphenylmethane and triphenylmethane with *tert*-butyl hydroperoxide (TBHP) [8] and in Friedel-Crafts benzylation of benzene [9]. Iron coordinated to 1,3,5-benzenetricarboxylate (BTC), [Fe(BTC)] metal-organic framework, has been commercialized by BASF under the trade name of Basolite F300. Although the exact crystal structure of Fe(BTC) is still unknown, it likely has a structure similar to that of MIL-100 (Fe). [Fe(BTC)] is an effective catalyst for aerobic oxidations of cyclooctane [10] and styrene [11]. In turn, MIL-100 (Cr) operates effectively as a Lewis acid catalyst in various organic transformations [12]. MIL-101 (Cr) is able to catalyze the cyanosilylation of benzaldehyde [13], carboxylation of epoxides [14], benzylic oxidation of tetralin [15], sulfoxidation of thioethers with H_2O_2 [16], oxidation of cyclohexane [17], and allylic oxidation of alkenes with TBHP [18] or O_2 [19].

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Dicyclopentadiene (DCPD) is generally formed via the combination of cyclopentadiene (CPD) molecules through the Diels-Alder reaction and is composed of two stereoisomers, namely, the endo- and exo-isomers; the former constitutes approximately 99.5% and the latter only 0.5% [20]. DCPD has been widely used as the monomer or feedstock for various resins, rubbers, and high-energy fuels [21]. Recently, exo-DCPD has attracted increasing interest because of its superior performance in the preparation of polymers and high-energy fuels. For example, the ring-opening metathesis polymerization (ROMP) of exo-DCPD arises much faster than that of endo-DCPD, and the produced polymer is more rigid [22]. In addition, the hybrid of exo-DCPD, JP-10, which is a widely used missile fuel, shows much better low-temperature performance than does hydrogenated endo-DCPD [21]. Therefore, it is necessary to transform the endo-isomer to the exo-isomer.

The isomerization of endo- to exo-DCPD is not new, but the efficiency and strategies must be improved. Bartlett and Goldstein first reported a two-step method [23]. The double bond in the norbornene unit of endo-DCPD is mixed with HI, and then the HI is eliminated with alcoholic potassium hydroxide, whereby the endo-structure is converted into its exo-counterpart. Nelson and Kuo modified this process by using HBr to replace HI; this has been widely accepted for laboratory preparations [24]. Herndon et al. found that some exo-DCPD is formed when endo-DCPD is heated at 205 °C for a prolonged period [25]. Baldwin suggested a dissociation-recombination mechanism to explain this phenomenon [26]. Zhang et al. conducted this transfer at a milder temperature but higher pressure, and the yield of exo-DCPD was significantly improved [27]. However, the use of solvents and reagents brings about environmental concerns; also, the operation is too complicated for industrial applications. Hence, Bakke and Morten presented a one-step catalytic isomerization of endo-

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DCPD in gas phase over Pt-containing silica alumina catalysts, but this resulted in extremely low yields [28].

Thus, the exploration of new heterogeneous catalysts that are efficient under mild reaction conditions without solvents remains highly desirable. This paper presents the solvent-free isomerization of endo- to exo-DCPD using MOF catalysts, MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr). The synthesis of MIL catalysts is much easier and more convenient than those of conventional zeolitic materials. To improve the understanding of the isomerization, the influence of the acidic properties of the MIL catalysts on the synthesis of exo-DCPD was evaluated. In addition, the effects of the reaction time, reaction temperature, and catalyst loading are discussed. The MIL catalysts were subjected to a recycle test and hot catalyst filtration in order to examine their stabilities.

2. Experimental

2.1. Materials

Iron powder (>99%), metallic chromium (>99%) and other chemicals (>99%), which are used as raw materials to prepare metal-organic frameworks, were purchased from Aldrich. Endo-dicyclopentadiene of 98% purity (Aldrich) was used without further purification.

2.2. MOF synthesis and characterization

MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) were synthesized according to the literature [5], [7], [9] and [16] with some modifications. For details, see the Electronic Supplementary Information.

2.3. Isomerization of endo- to exo-DCPD

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The isomerization of the endo- to the exo-dimer was carried out in a 100-mL glass reactor equipped with a magnetic stirrer and condenser (Scheme 1). In a typical reaction, the catalyst and reactant were charged into the reactor. When the desired temperature was attained, the reaction was initiated by stirring under atmospheric pressure. The products and reactant were identified using a gas chromatograph (BRUKER 450-GC) equipped with a flame ionization detector (FID) and a capillary column (HP-5, (5% phenyl)-methylpolysiloxane). The conversion was calculated based on the assumption that endo-DCPD was the limiting reactant using an internal standard method with benzene as the standard.

3. Results and discussion

3.1. Characterization of MIL catalysts

The as-synthesized MILs were characterized by XRD, FT-IR, low N_2 sorption measurements, and TGA. The XRD patterns (Fig. S1) [7], [9] and [16] and FT-IR spectra (Fig. S2) [29] and [30] of all of the materials were in accordance with the literature. The N_2 sorption isotherms shown in Fig. S3 gave BET surface areas of 1976.5 $m^2 g^{-1}$, 1599.5 $m^2 g^{-1}$, 2686.3 $m^2 g^{-1}$, and 2276.1 $m^2 g^{-1}$ for MIL-100 (Fe), MIL-100 (Cr), MIL-101 (Fe), and MIL-101 (Cr), respectively. As shown in Fig. S4, the TGA curves of the MILs demonstrate that all of the samples show good thermal stability up to 350 °C, which is much higher than the reaction temperature for the isomerization of endo- to exo-DCPD.

The differences in the acidic properties of the MIL catalysts were evaluated based on the TPD of NH_3. The NH_3-TPD profiles of the MIL catalysts are shown in Table 1 and Fig. S5. These show that the acidity can be classified into two groups [31]: a weak-to-medium group,

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323–523 K; and a strongly acidic group, 473–623 K. Table 1 also summarizes the observed and calculated metal content as active center in MILs, amount of metal (calculated value) are 19.81 (27), 19.11 (26), 16.73 (24) and 16.53 (23) wt % in MIL-100 (Fe), MIL-100 (Cr), MIL-101 (Fe), and MIL-101 (Cr), respectively. This difference in the metal content from the calculated and observed ones is most likely due to the presence of the unreacted linkers and solvent molecules inside the pores of the MOF. The presence of extra molecules in the MILs was evident from the regular degradation pattern of TGA also (Fig. S4) [32].

3.2. Reactivity of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) catalysts

The effects of the structures (different metals) of the Fe- and Cr-containing MIL-100 and MIL-101 catalysts on the solvent-free isomerization of the endo- to the exo-dimer were studied under atmospheric pressure over a reaction time of 3 h at 140 °C (Table 2). In the absence of a catalyst, the conversion of endo-DCPD was limited to 1.0% with 0% selectivity for the exo-dimer (Table 2, entry 1). However, the MIL catalysts exhibited improved catalytic performances for the isomerization of endo- to exo-DCPD. For comparison under the similar reaction condition, the catalytic activities of reported zeolite materials, Hβ and HY, are given in Table 2, entries 2 and 3. The results indicated that the MIL catalysts showed higher selectivity toward exo-DCPD than did the zeolite catalysts even though conversion of endo-DCPD remained higher for the Hβ and HY catalysts.

The MIL catalysts showed disparities in their catalytic activities depending on the number of acid sites. MIL-100 (Fe) was found to be the most efficient catalyst, showing 17.3% conversion of endo-DCPD and 48.6% selectivity for exo-DCPD (Table 2, entry 4) under the employed reaction conditions. The other MOFs, MIL-100 (Cr), MIL-101 (Fe), and

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MIL-101 (Cr), were also active, showing conversions of 7.3% (Table 2, entry 6), 4.3% (Table 2, entry 7), and 4.2% (Table 2, entry 8), respectively, with similar selectivity. As revealed in Table 1, MIL-100 (Fe) owns a greater number of total acid sites, and this catalyst displayed better activity than did the other MIL catalysts. The catalysts arranged in order of isomerization activity are MIL-100 (Fe) > MIL-100 (Cr) > MIL-101 (Fe) > MIL-101 (Cr), which corresponds to the number of acid sites in each catalyst (MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) exhibited the order of total acid site such that: MIL-100 (Fe) (3.60 mmol g^{-1}) > MIL-100 (Cr) (3.02 mmol g^{-1}) > MIL-101 (Fe) (2.52 mmol g^{-1}) > MIL-101 (Cr) (2.47 mmol g^{-1})).

Moreover, the reactivity of the catalysts was evaluated based on the acetalization [33] of benzaldehyde with ethanol, which is a reaction catalyzed solely by acidic centers. Acetalization was performed via the reaction between 10 mmol benzaldehyde and 20 mmol ethanol without solvent for 2 h at 60 °C using 1 wt% of MIL catalysts to yield 1,1-diethoxymethylbenzene. The amount of product was estimated using gas chromatography to find the initial rate (r_o) value for acetalization. The results of acetalization using catalysts with different acid pairs are presented in Fig. 1. The initial rates of reaction for MIL-100 (Fe), MIL-100 (Cr), MIL-101 (Fe), and MIL-101 (Cr) were 1.94, 1.28, 0.71, and 0.53 mmol min^{-1} g^{-1}, respectively. Thus, the relative reactivities are consistent with those derived from the isomerization of endo- to exo-DCPD.

As is clear from the BET analysis, the MIL-101 (Fe, Cr) catalysts exhibited higher surface areas than MIL-100 (Fe, Cr). However, MIL-100 (Fe, Cr) performed better as catalysts for the endo- to exo-DCPD isomerization than did MIL-101 (Fe, Cr). This can be attributed to the higher number of weak-medium acid sites in the MIL-100 (Fe, Cr) catalysts;

between them, the Fe-containing MIL displayed more activity than its Cr counterpart, which supplements the above rationale. In a previous report [34], the catalytic activity in the isomerization of endo- to exo-DCPD over zeolite catalysts strongly depended on the acidic properties; weak acid sites play a more important role in the isomerization of endo-DCPD.

From these observations, we surmise that in this endo- to exo-DCPD isomerization, which is a liquid-phase reaction, the acidic properties play a more significant role than does the surface area of the catalyst. Should this observation be generalized, it proposes syntheses of MOFs with tunable acid sites rather than focusing on the surface features for catalytic purposes, which generally works through opportunistic catalysis at the struts, nodes, defect sites, or some combination thereof.

3.3. Parameter Study

Fig. 2 shows the effects of the reaction temperature on the isomerization of endo- to exo-DCPD in the presence of MIL-100 (Fe). The conversion of endo-DCPD significantly increased as the temperature increased from 100 to 180 °C. The selectivity toward exo-DCPD was maintained with temperature at approximately 49.0% for MIL-100 (Fe) at 140 °C; however, the selectivity decreased sharply when the temperature exceeded 140 °C. When the temperature was above 140 °C, exo-DCPD reversibly decomposed into CPD [26]. Moreover, in this process, thermal oligomerization (TCPD/TeCPD) of endo-DCPD has been reported to be one of the main factors responsible for the low selectivity toward the exo-dimer [26] and [34].

The reaction time also had a prominent influence on the catalytic activity in the isomerization of endo- to exo-DCPD. The effect of reaction time on the isomerization was

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studied by keeping the reaction conditions constant (at 140 °C under atmospheric pressure). As shown in Fig. 3, increased reaction time promoted the conversion of endo-DCPD; however, the selectivity for exo-DCPD after 4 h decreased, likely because of the oligomerization of exo-DCPD. A reaction time from 2 to 4 h appears to be more favorable for the isomerization of the endo- to the exo-dimer.

The effect of the catalyst loading on the yield was investigated using MIL-100 (Fe) at 140 °C for 3 h under atmospheric pressure. As shown in Fig. 4, the selectivity for exo-DCPD and the endo-DCPD conversion increased continuously as the catalyst loading increased up to 5 wt%. Further increase in the concentration of MIL-100 (Fe) did not significantly enhance the conversion, probably due to the presence of excess catalyst that resulted in restricted dispersion in the reaction mixture, which eventually limited mass transfer between the active sites and the reactants [35].

The stability of the MIL-100 (Fe) catalyst was evaluated through recycling experiments. For each cycle, the used catalyst was separated by filtration, washed with ethanol to remove products adhering to the catalyst surface, dried at room temperature, and then reused directly for the next run without regeneration. The activity of the reused MIL-100 (Fe) catalyst is summarized in Table 3. Although the conversion of endo-DCPD decreased slightly with the catalyst used for three cycles, the selectivity toward exo-DCPD was nearly identical to that achieved with the fresh catalyst. To determine whether the active metal center underwent leaching from the MIL-100 (Fe) during the recycling test, XRD analysis of fresh MIL-100 (Fe) catalyst and that used for three cycles was performed (Fig. 5). The characteristic peaks of MIL-100 (Fe) were similarly present for the recycled and fresh catalysts and the ICP-OES confirmed that no significant amount of iron (≤ 0.2 ppm) was leached into the reaction

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mixture. Therefore, it can be concluded that the MIL-100 (Fe) catalyst could be recycled for up to three consecutive cycles without considerable loss of its initial activity. However, some new peaks can be found in this sample, especially the large peak at around 16 degree to be the result of the interaction of remaining reactant or product with some of the metal sites within the pores during the repeated uses. In order to check for a possible contribution of homogeneous catalytic action from active metal leached into solution, a hot catalyst filtration test was performed after 3 h of reaction. As shown in Fig. 3, no further endo-DCPD conversion in the filtrate occurred after catalyst removal at the reaction temperature, indicating that catalysis was not due to leached species.

4. Conclusions

The MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) catalysts were successfully synthesized and characterized according to previous literature. The MIL structures are easily synthesizable, green, and reusable catalysts for solvent-free isomerization of endo- to exo-DCPD with higher selectivity. The catalytic activity in the isomerization depended on the nature of the active metal site. Among the MIL catalysts, MIL-100 (Fe) exhibited the highest catalytic activity in the isomerization of endo- to exo-DCPD under mild reaction conditions due to the higher number of weak-medium acid sites, which play a more important role in the isomerization of endo-DCPD. The catalyst was also easily recovered and reused without considerable loss of the initial activity. The solvent-free isomerization of the endo- to the exo-dimer is distinguished by various advantages such as environmental friendliness, simple work-up process, and easy availability of materials.

Acknowledgements

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List of Tables

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Table 1 The amount of acid site and metal content of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr)

Catalyst	NH_3-TPD (mmol g^{-1})			Metal content [c] (%) (calcd)
	Weak-medium acid [a]	Strong acid [b]	Total (calcd)	
MIL-100 (Fe)	3.45	0.15	3.60 (3.2)	19.81 (27)
MIL-100 (Cr)	2.75	0.27	3.02 (3.3)	19.11 (26)
MIL-101 (Fe)	1.13	1.39	2.52 (2.9)	16.73 (24)
MIL-101 (Cr)	0.92	1.55	2.47 (2.9)	16.53 (23)

[a] 323 ~ 523 K

[b] 473 ~ 623 K

[c] by ICP-OES

Table 2 Reactivity of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr)

Entry	Catalysts	Conversion (%)	Selectivity (%)	Reference
1	Blank	< 1.0	0.0	This work
2	Hβ zeolite [a]	20.5	38.3	33
3	HY zeolite [a]	11.2	20.5	33
4	MIL-100 (Fe)	17.3	48.6	This work
5	MIL-100 (Fe) [b]	20.3	40.5	This work
6	MIL-100 (Cr)	7.3	41.2	This work
7	MIL-101 (Fe)	4.3	40.5	This work
8	MIL-101 (Cr)	4.2	40.7	This work

Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt%, Temp. = 140 ^oC, Reaction time = 3 h

[a] 25g endo-DCPD, Cat./endo-DCPD = 5 wt%, Temp. = 150 ^oC, Reaction time = 3 h

[b] 5g endo-DCPD, Cat./endo-DCPD = 5 wt%, Temp. = 150 ^oC, Reaction time = 3 h

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Table 3 Recycling test of MIL-100 (Fe) on the isomerization of endo- to exo-DCPD

Entry	Recycle	Conversion (%)	Selectivity (%)
1	Fresh	17.3	48.6
2	1st	16.4	49.1
3	2nd	14.3	48.3
4	3rd	10.7	46.0

Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt% MIL-100 (Fe), Temp. = 140 ^{o}C, Reaction time = 3 h

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List of scheme and figures

Scheme 1 Isomerization of endo- to exo-DCPD.

Fig. 1 Relative activity of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) on the acetalization of benzaldehyde with ethanol.

[Reaction conditions: 10 mmol of benzaldehyde with 20 mmol of EtOH (1 wt% of cat., 60 °C, 2 h)]

Fig. 2 Effect of reaction temperature on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt% MIL-100 (Fe), Reaction time = 3 h]

Fig. 3 Effect of reaction time on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt% MIL-100 (Fe), Temp. = 140 ^{o}C]

Fig. 4 Effect of catalyst amount on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = x wt% MIL-100 (Fe), Temp = 140 ^{o}C, Reaction time = 3 h

Fig. 5 XRD pattern of (a) fresh and (b) 3rd reused MIL-100 (Fe).

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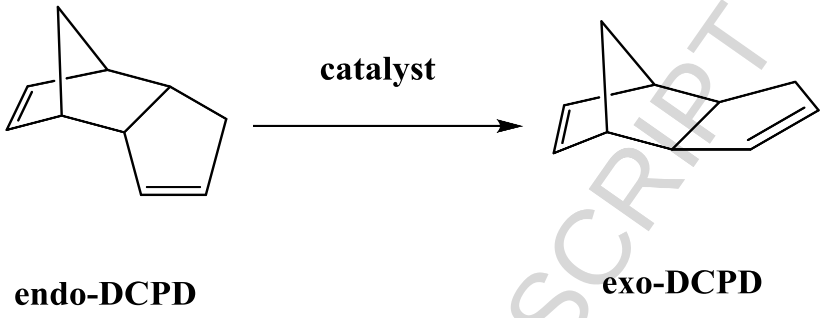

Scheme 1 Isomerization of endo- to exo-DCPD.

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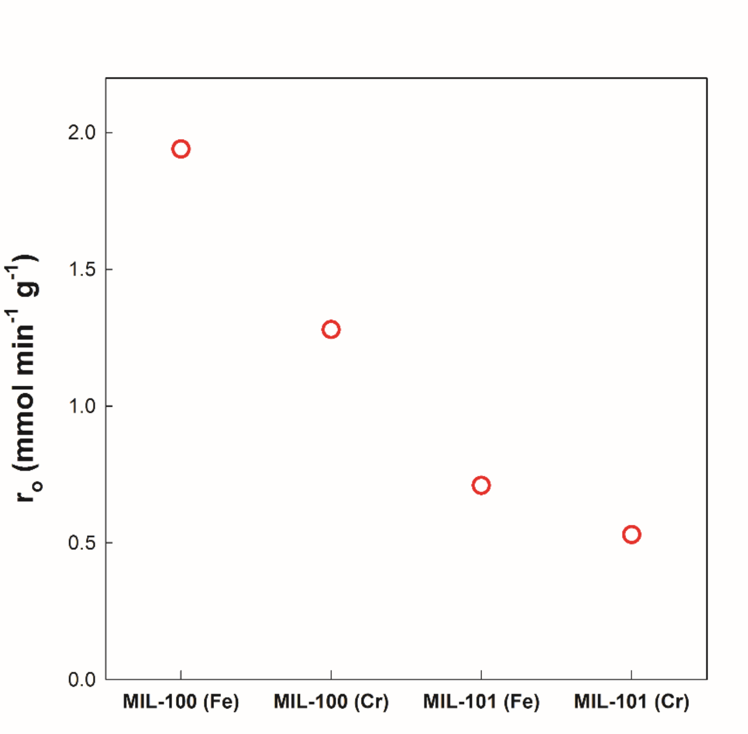

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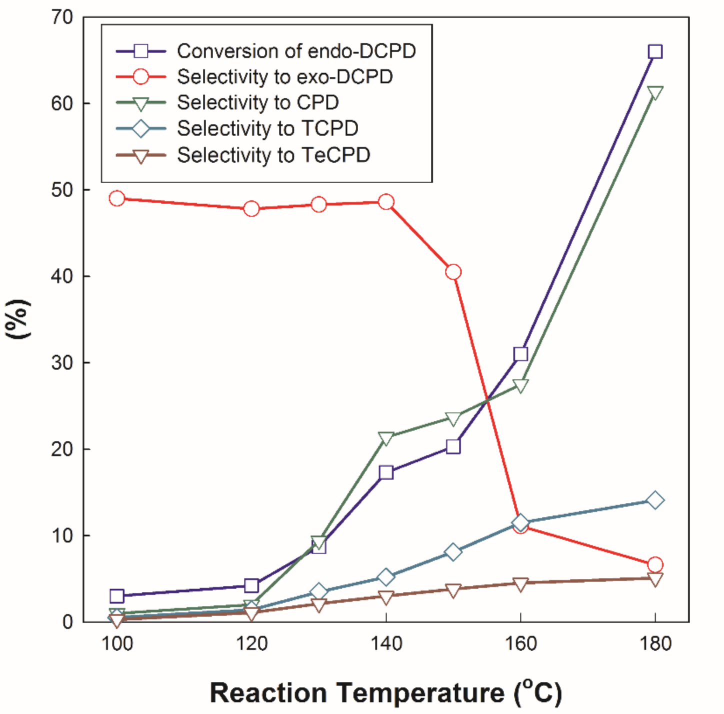

Fig. 2 Effect of reaction temperature on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt% MIL-100 (Fe), Reaction time = 3 h]

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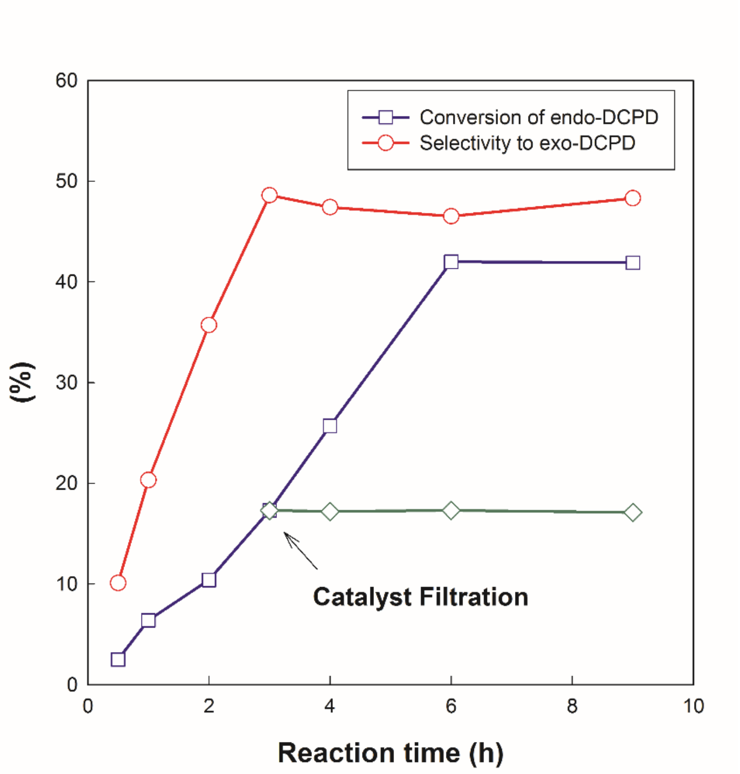

Fig. 3 Effect of reaction time on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = 5 wt% MIL-100 (Fe), Temp. = 140 ^{o}C]

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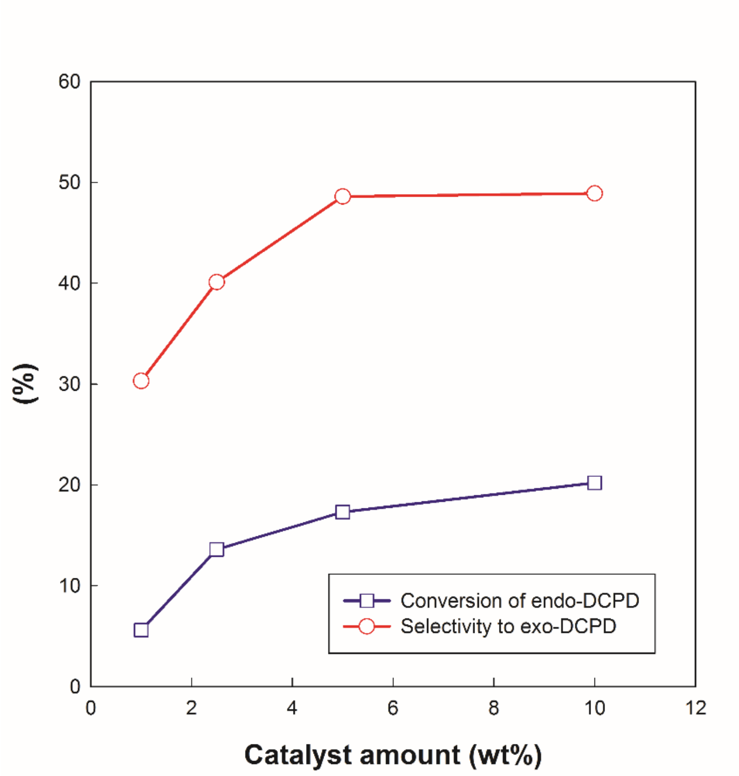

Fig. 4 Effect of catalyst amount on the isomerization of endo- to exo-DCPD.

[Reaction conditions: 5g endo-DCPD, Cat./endo-DCPD = x wt% MIL-100 (Fe), Temp = 140 ^{o}C, Reaction time = 3 h]

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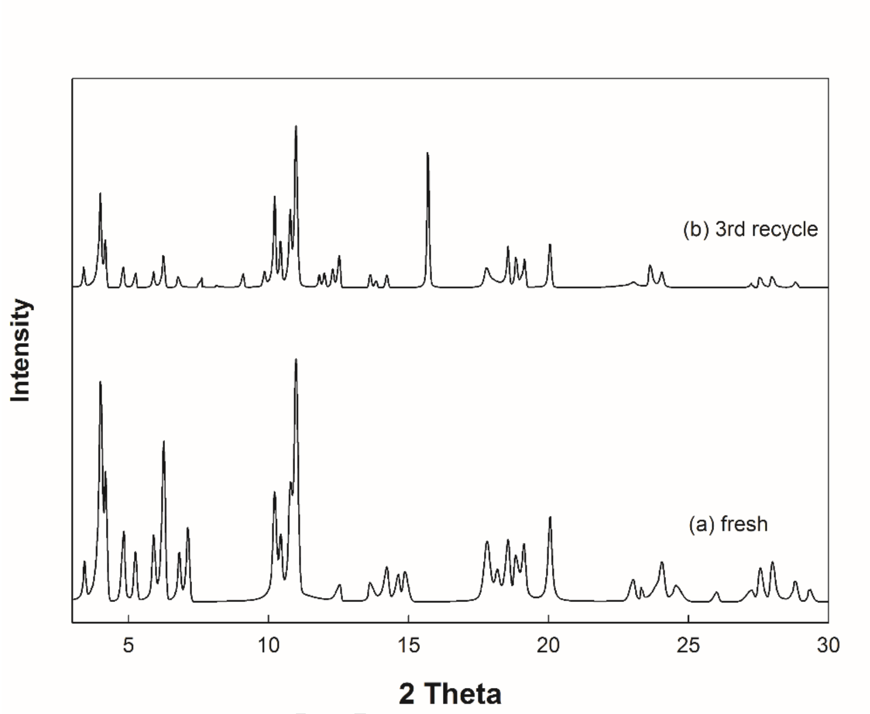

Fig. 5 XRD pattern of (a) fresh and (b) 3rd reused MIL-100 (Fe).

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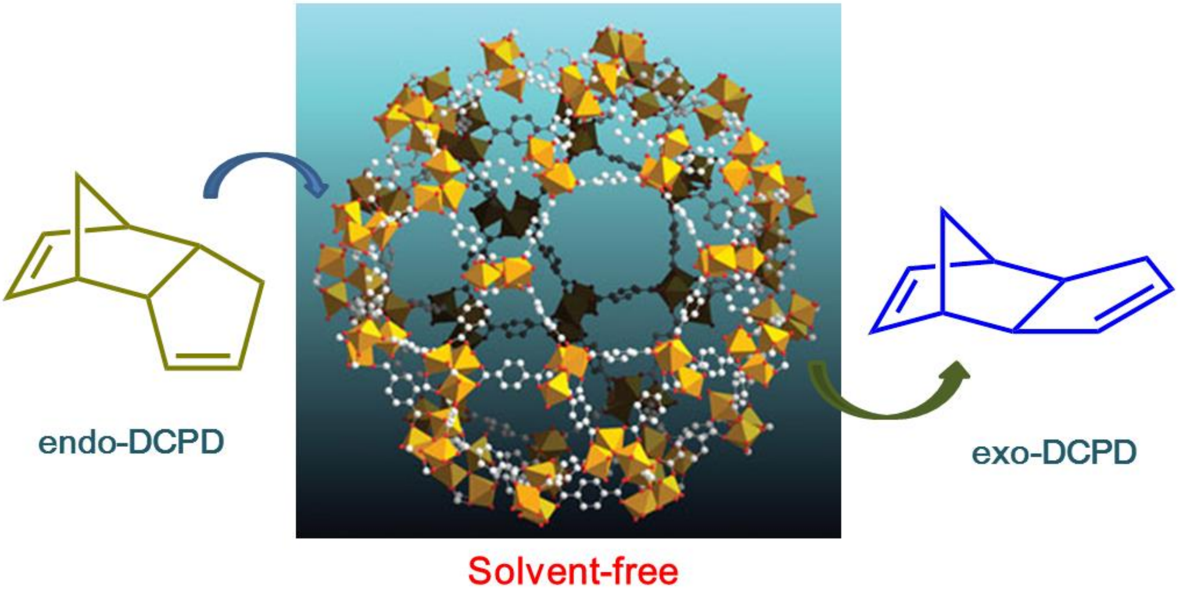
Graphical abstract



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Highlights

- MILs catalysts were successfully synthesized and characterized.
- MILs have been confirmed its potential as catalyst for the isomerization.
- The acidic properties of MILs play a more significant role in the isomerization.
- MILs were easily reused without any considerable loss of the initial activity.

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