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Hf-MOF catalyzed Meerwein–Ponndorf–Verley (MPV) reduction reaction: Insight into reaction mechanism

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ABSTRACT

Hf-MOF-808 exhibits excellent activity and specific selectivity on the hydrogenation of carbonyl compounds *via* a hydrogen transfer strategy. Its superior activity than other Hf-MOFs is attributed to its poor crystallinity, defects and large specific surface area, thereby containing more Lewis acid-base sites which promote this reaction. Density functional theory (DFT) computations are performed to explore the catalytic mechanism. The results indicate that alcohol and ketone fill the defects of Hf-MOF to form a six-membered ring transition state (TS) complex, in which Hf as the center of Lewis stearic acid coordinates with the oxygen of the substrate molecule, thus effectively promoting hydrogen transfer process. Other reactive groups, such as $-NO_2$, C = C, -CN, of inadequate hardness or large steric hindrance are difficult to coordinate with Hf, thus weakening their catalytic effect, which explains the specific selectivity Hf-MOF-808 for reducing the carbonyl group.

1. Introduction

Meerwein – Ponndorf – Verley (MPV) reduction is one of the traditional technologies for redox reactions, which can realize the selective hydrogenation of carbonyl groups through hydrogen transfer between ketones (aldehydes) and alcohols [1]. MPV reaction has been widely applied in various organic synthesis to produce useful chemicals, especially in the fields of asymmetric synthesis and biomass conversion.

Compared with the hydrogenation under H_2 atmosphere, the MPV reduction that use secondary alcohol as hydrogen source seems to be a milder hydrogenation method. The catalysts used in traditional MPV reactions can be divided into two types. One type is various metal oxides, such as iron [2], magnesium [3], aluminum [4] and so on. Although such metal oxides can be easily obtained, their poor catalytic efficiency often leads to the requirement of harsh reaction conditions, such as high temperature and pressure. The other type is precious metal supported catalysts, such as ruthenium [5], platinum [6], palladium [7], rhodium [8] and so on, which require mild reaction conditions and show higher catalytic efficiency. However, the problems brought by precious metal supported catalysts such as the costs and the impact on the environment, also need to be considered. In recent years, several

non-precious metal-based catalysts derived from MOF $[9\mathchar`-14]$ have been developed for MPV reactions.

Metal-organic frameworks (MOFs) suitable for catalysis because of their highly tunable porosity, high density of accessible metal sites, high specific surface area and good designability [15–20]. Among these MOF derived catalysts, Hf-MOF_S show excellent performance in the MPV reduction reactions [21–25]. Ideally, the highly active Lewis acid sites in Hf-MOF_S such as Hf-MOF-808 and Hf-UiO-66, are occupied by organic ligands. In fact, the crystal structures of UiO-66 or MOF-808 are rarely ideal and the coordination modulator can be added during the synthetic process, which make the materials with large number of defects [26,27]. The exposed Hf-O bond in these defects can be used as ideal Lewis acid-base sites and applied in the catalytic hydrogen transfer reactions [27–35]. In addition, the ordered pore structure, large specific surface area and good thermal stability of Hf-MOF derived materials are also conductive to catalytic reactions.

Noyori et al. [36] used the Ru complex to explore the mechanism of catalyzing the hydrogen transfer reaction of alcohols and ketones. They believe that this approach involves metal hydride intermediates. Komanoya et al. [37] compared ZrO_2 with Nb₂O₅ and TiO₂. The high catalytic performance of ZrO_2 for MPV reduction is attributed not only

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to the strength of Lewis acid centers, but also to the large amount of base sites. Han's group [23] reported the mechanism of using a porous catalyst formed by hafnium-phytic acid (Hf-phy) to catalyze the hydrogen transfer reduction reaction. $Hf^{4+}-O^{2-}$ and Hf^{4+} in Hf-phy activate the hydroxyl group on isopropanol and the aldehyde group on the substrate respectively, and then the activated aldehyde group interacts with isopropanol to form a six-membered ring intermediate. Gonell et al. [38] reported the co-adsorption of cyclohexanone and propoxide on two neighboring surface Zr atoms leading to a seven-membered ring TS, which is different from the previous reaction model, in which the two reactant fragments adsorb on the same Zr center [23,37]. Although some previous works [21-25] discussed the hydrogen transfer ability of Hf-MOFs, no related research addressed the selectivity of its catalytic transfer hydrogenation. In addition, the mechanism of Hf-MOFs catalyzing the transfer hydrogenation of ketones (aldehydes) still needs further study. Rojas-Buzo et al. [25] reported that Hf-MOF-808 is a direct hydrogen transfer, instead of a sequential metal hydride formation and subsequent carbonyl reduction. At the same time, it is proposed to form a six-membered intermediate between alcohol, carbonyl compound and Lewis acid center.

This paper found that even in the presence of other easily reduced groups (such as halogens, nitriles, nitro groups and unsaturated carbon moieties), Hf-MOF can achieve hydrogenation of carbonyl groups with high efficiency and specific selectivity (>99%). The catalyst has good stability, and the catalytic performance remains basically unchanged after being recycled five times. Compared with Hf-UiO-66, Hf-MOF-808 has more defects, so it has more active Lewis acid-base sites to promote this hydrogen transfer reaction. Furthermore, we perform DFT computation to study catalytic mechanism of Hf-MOF-catalyzed MPV reaction. A cluster model containing six Hf (IV) ions are employed to describe the reaction site, from which the TS and product are derived.

2. Experimental

2.1. General

All chemical reagents are obtained from commercial suppliers and used without further purification. GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μ m × 0.25 μ m, carrier gas: H₂, FID detection. The crystal structure of the synthesized catalysts was recorded by X-ray diffraction (XRD) using a D8ADVANCED X-ray diffractometer, employing a scanning rate of 0.1 s⁻¹. Scanning electron microscopy (SEM) spectras were taken using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold. BET surface areas were recorded with N₂ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2920 instrument. Before measurements, the samples (> 100 mg) were degassed at 150 °C for 12 h. The Raman spectra were obtained using confocal Raman spectroscopy (inVia-Reflex) employing 785 nm radiation (3 mW).

2.2. Synthesis of Hf-MOFs

2.2.1. Hf-MOF-808

A mixture of HfCl₄ (160 mg, 0.5 mmol), 1,3,5-benzenetricarboxylic acid (110 mg, 0.5 mmol), DMF/formic acid (20 mL/20 mL) was sonicated for 30 min and then added to an autoclave vessel and heated at 120 $^{\circ}$ C for 48 h. After reaction, the mixture was cooled down to room temperature. The resulting solid was filtered and washed with an excess of ethanol. Finally the obtained solid was activated at 80 $^{\circ}$ C in vacuum for 12 h.

2.2.2. Hf-UiO-66-NH2

HfCl₄ (160 mg, 0.5 mmol) and 2-aminoterephthalic acid (90 mg, 0.5 mmol) were added into a 30 mL of DMF solution, followed by adding 1.5

mL of formic acid. After ultrasonication and dissolution, The mixture was added to an autoclave vessel and heated at 120 °C for 48 h.After reaction, the mixture was cooled down to room temperature. The resulting solid was filtered and washed with an excess of ethanol. Finally the obtained solid was activated at 80 °C in vacuum for 12 h.

2.2.3. Hf-UiO-(OH)₂

HfCl₄ (160 mg, 0.5 mmol) and 2,5-dihydroxyterephthalic acid (99 mg, 0.5 mmol) were added into a 30 mL of DMF solution, followed by adding 1.5 mL of formic acid. After ultrasonication and dissolution,The mixture was added to an autoclave vessel and heated at 120 °C for 48 h. After reaction, the mixture was cooled down to room temperature.The resulting solid was filtered and washed with an excess of ethanol. Finally the obtained solid was activated at 80 °C in vacuum for 12 h.

2.2.4. Hf-UiO-66

HfCl₄ (160 mg, 0.5 mmol) and 1,4-benzenedicarboxylic acid (83 mg, 0.5 mmol) were added into a 30 mL of DMF solution, followed by adding 1.5 mL of formic acid. After ultrasonication and dissolution,The mixture was added to an autoclave vessel and heated at 120 $^{\circ}$ C for 48 h. After reaction, the mixture was cooled down to room temperature. The resulting solid was filtered and washed with an excess of ethanol. Finally the obtained solid was activated at 80 $^{\circ}$ C in vacuum for 12 h.

2.3. The general procedure for the selective hydrogenation of ketones or aldehydes

A mixture of 0.2 mmol of carbonyl compound and 20 mg of Hf-MOF was added to isopropanol (1 mL), and the mixture was stirred and reacted at 120 °C for 12 h under N₂ atmosphere. After the reaction was completed, Hf-MOF was isolated from the solution by centrifugation and wash by EtOAc (1 mL \times 3). Then the resulted solid was reused for another reaction cycle directly. The organic layer was collected and removed in *vacuo* to afford the crude product, which was analyzed by GC and GC-MS.

2.4. Computational Details

The Hf-MOF cluster model containing 6 Hf atoms is employed in our computation, which is based on the UiO-66 structure 1406507(Zr) with Zr replaced by Hf. The terephthalic acid ligands were replaced by formic acid to obtain the initial structural model. All DFT calculations were performed at the B3LYP level [39,40] using Guassian 09 W software package [41]. The LANL2DZ and 6-31 g(d) basis sets are used for Hf and rest atoms, respectively.

Two formate ligands coordinated to the same Hf (IV) were removed so that cyclohexanone and isopropanol can be introduced as substrates. After optimizing the reactant, we used the multi-coordinate driven (MCD) method [42] to drive the reactant to the product using four active coordinates, namely the distances of C1-H1, C2-H1, O2-H2, and O1-H2. The resulting product structure was further optimized.

With the optimized reactant and product structures available, we used MCD method [42] to find a low barrier reaction path connecting the reactant and product [43]. As long as the minimum energy path is smooth and continuous, the structure corresponding to the maximum energy along this reaction path provides an approximate TS structure. The energy difference between the TS and the reactant state yields an estimate of the reaction barrier.

3. Results and discussion

3.1. Catalytic performance studies

The hydrogen transfer reduction of *p*-nitroacetophenone was selected as the model reaction. After screening reaction time, temperature and catalyst loading, the reaction can be provided >99% yield of **2a**

Table 1

The catalytic performance of different Hf-MOFs a.



Conditions: 1a or 1b (0.5 mmol), catalyst (20 mg), isopropanol (1 mL), 120 °C (), 3 h.

^b The yields and selectivity were determined by GC using dodecane as the internal standard.

catalyzed by 20 mg of Hf-MOF-808 at 120 °C for 3 h (Table S1 in Supporting information). Both catalytic efficiency and selectivity of all four Hf-MOFs were excellent (Table 1, entries 1-4). Cinnamic aldehyde was selected as the substrate to screen Hf-MOFs (entries 5-8). It can be indicated that all four Hf-MOFs show specific selectivity (>99%) and Hf-MOF-808 shows the best catalytic efficiency in the hydrogenation of cinnamic aldehyde (85% yield).

After that, we applied the Hf-MOF-808 as the catalyst to explore the substrate scope of the transfer hydrogenation of ketones or aldehydes (Table 2). Hf-MOF-808 shows excellent catalytic efficiency and specific selectivity towards the substrates that contain both carbonyl groups and other easily reduced groups, such as nitro group, C = C bond and cyano group (2a-2f). The substituent effects of cinnamic aldehydes in this transformation were also investigated. Excellent yields could also be obtained when the ortho position of the benzene ring in substrates is substituted (2k and 2l). For the substrates with substituents at α -carbon, the steric hindrance around the carbonyl group couldn't weaken the catalytic efficiency of Hf-MOF-808 (2h-2 j). However, in the cases of chalcone and 4-chlorochalcone, the excessive hindrance indeed limit the hydrogenation of carbonyl group. In addition, good yields could also obtained when the substrate with heterocycle was used, such as acrolein furan (2 m).

According to the XRD results (Fig. 1), the skeleton of UiO-66 is almost the same as reported results ($2\theta = 7.37^{\circ}$ (111), 8.52° (002), 12.06° (022), 14.78° (222), 17.08° (004), and 25.74° (006) & (244)) [13,14], which shows good crystallinity. However, there are more and weaker peaks in the XRD pattern of Hf-MOF-808, indicating its poor crystallinity. It can be attributed to the use of formic acid during the synthetic process of Hf-MOF-808, and the added formic acid could coordinate with Hf and occupied the coordination sites of trimesic acid, which distorts the framework of MOF and leads to significant lattice defects or vacancies [44]. From the SEM image of Hf-MOF-808 (Fig. 2), it can be indicated that the surface of Hf-MOF-808 is abnormally rough and amorphous, which may be caused by the introduction of defects. The rough surface is easier to absorb the substrates and promote the reaction.

The porosity of Hf-MOF-808 was also studied by nitrogen adsorption-desorption isotherm (Fig. 3). The N₂ adsorption-desorption isotherm shows the hysteresis loop of type IV, which is the characteristics of micro/mesoporous materials. In addition, the BET surface area of Hf-UiO-66 is 584 m^2/g [45], which is lower than that of Hf-MOF-808 (621 m^2/g). Compared with Hf-UiO-66, the crystal structure of Hf-MOF-808 has more defects, which lead to the slightly increased

Table 2

The substrate scope of I	HI-MOF-808 catal	yzea MPV	reaction
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Entry	Substrate	Product	Yield (%) ^b
1	0	ОН	>99
	0 ₂ N	O ₂ N	
2		ОН	85
3	1b	2b	94
5			71
	1c	2c	
4	0 ₂ N	O ₂ N OH	>99
5	NC O	2d NC	>99
6	1e O CN	2e OH CN	92
7	1f O ₂ N	2f O2N	>99
8	1g Br O	2g Br OH	>99
9	1h Cl	2h Cl OH	>99
10		2і	>99
11	1j NO ₂	2j NO ₂ OH	>99
12		2k O OH	>99
13			80
14	1m F0	2 т FОн	87
15	1n	2n OH	11 ^c
16			10 ^c

^aConditions: substrate (0.5 mmol), catalyst (20 mg), isopropanol (1 mL), 120 °C, 3 h.

 $^{\rm b}$ The yields and selectivity were determined by GC using dodecane as the internal standard.

^c The reaction time was 12 h.



Fig. 1. XRD patterns of the UiO-66 and Hf-MOF-808.

surface area and almost unchanged pore volume. At the same time, large number of Lewis acid-base sites are formed due to the introduction of defects, which promote the contact between the catalyst and substrates and thereby improve the catalytic performance of Hf-MOF-808.

The recyclability is one of the key factors in evaluating the performance of heterogeneous catalysts [46,47]. In order to verify the recyclability of prepared Hf-MOF-808, *p*-nitrobenzaldehyde as substrate to react at 120 °C for 1 hours was selected as model reaction (Fig. 4). After completion of the reaction, the catalyst was recovered by centrifugal and washed with EtOAc. Then it was reused in the next run directly. After 5 cycles, the yield remained constant in the first three runs, decreasing by approximately 12% for the rest of the recycles. The results indicated that Hf-MOF-808 was stable enough to maintain its own structure after five cycles. No obvious change in particle size of Hf-MOF-808 was found based on SEM images (Figure S1). The crystal structure of Hf-MOF-808 was further destroyed after 5 runs (Figure S2), and the BET surface area of the catalyst was reduced from $621 \text{ m}^2/\text{g}$ to $417 \text{ m}^2/\text{g}$ (Figure S3). Therefore, the decrease in catalyst activity of Hf-MOF-808 is mainly due



Fig. 4. Reusability experiments of Hf-MOF-808.



Fig. 2. SEM images of Hf-MOF-808.



Fig. 3. N₂ adsorption and desorption isotherm diagram and pore size distribution diagram of the Hf-MOF-808.



Fig. 5. The optimized Hf-MOF cluster.

to the decrease in the specific surface area of the catalyst during the recovery process.

3.2. Density functional theory calculations

The Hf-MOF-catalyzed MPV reduction mechanism is further explored by DFT computations. In the optimized Hf-MOF cluster (Fig. 5), the six Hf (IV) ions form an octahedral arrangement, in which each Hf atom is coordinated with 6 O atoms, and each μ -O or μ -OH coordinated with 3 Hf atoms.

During the optimization of the reactant structure, both substrates, which replace two formic acid ligands, are coordinated to Hf (IV) forming Hf-O bond, while the H2 atom on the hydroxyl group of isopropanol is gradually transferred to the μ -OH atom (O1 atom) connected to Hf (IV) (Fig. 6a). Consequently, the two substrates are ideally positioned for the subsequent reaction. In the optimized product structure (Fig. 6b), the H1 atom on the C1 atom of the isopropanol fragment has been transferred to the C2 atom of the cyclohexanone carbonyl group, while the H2 atom on the μ -OH atom is transferred to the O2 atom of cyclohexanone. The isoacetone and cyclohexanol products are detached from Hf (IV) and leave the reaction system.

The potential energy profile along the reaction path computed from DFT is depicted in Fig. 7a. The reactant and product correspond to the two ends of the potential energy curve. The progress of the four active coordinates are shown in Fig. 7b. As the product transforming to the reactant, the distances between C2-H1 and O2-H2 increase, while the distances between C1-H1 and O1-H2 decrease. The transfer of H1 from isopropanol to cyclohexanone and that of H2 from µ-OH to the oxygen atom of cyclohexanone is synchronized. The maximum energy on the reaction path appears at $rc \approx 0.65$, and the corresponding structure provides an approximate TS (Fig. 8). In the TS, the proton H1 is located between C1 of isopropanol and C2 of cyclohexanone, and the distances are 1.36 Å and 1.35 Å, respectively, while the proton H2 is in the middle of O1 of Hf-MOF and O2 of cyclohexanone, the separations are 1.23 Å and 1.27 Å respectively. The TS is characterized by a six-membered ring containing the Hf (IV), O, α -C and proton H1 of the two substrate molecules, consistent with that proposed by by Komanoya et al. based on chemical intuition [37]. The energy barrier is about 190 kJ/mol. These results explain why Hf-MOF catalyst fail to catalyze the reduction reaction between many substrates containing nitro group or cyano group in Table 2. Theses substrates either have too large steric hindrance or contain reactive atoms not hard enough.



Fig. 6. Optimized structure of (a) the reactant. (b) the product.



Fig. 7. The reaction path obtained from the MCD method using four active coordinates. (a) Energy profile. (b) Progress of the four active coordinates.



Fig. 8. Approximate TS structure corresponding to the maximum energy point on the MCD reaction path.

4. Conclusions

In summary, Hf-MOF-808 exhibits excellent activity and selectivity on the hydrogenation of carbonyl compounds via a hydrogen transfer strategy owing to its poor crystallinity, defects and large specific surface area. The advantages of MPV reduction over Hf-MOF is including free of noble metal and high-pressure H₂, recyclable catalyst, high yields and specific selectivity. As revealed by DFT computations, defects formation is essential for the Hf-MOF catalytic power for MPV reaction. Only substrates of suitable sizes and containing hard reactive atoms like oxygen can be catalyzed. For suitable substrates, a six-membered ring TS in which Hf is a Lewis stearic acid site and μ -OH serve as a basic center is formed, thereby promoting the hydrogen transfer process. For other reaction systems, if the hardness of the reactive atom from substrate molecule is inadequate or the steric hindrance is too large, it is difficult to coordinate with Hf, resulting in a weakening of the catalytic effect.

CRediT authorship contribution statement

Yamei Lin: Investigation, Data curation, Writing - original draft. Qingxia Bu: Investigation, Software, Formal analysis. Jiaxian Xu: Investigation, Data curation, Writing - original draft. Xiao Liu: Investigation, Software, Formal analysis. Xueping Zhang: Investigation, Data curation, Writing - original draft. Guo-Ping Lu: Conceptualization, Methodology, Supervision, Writing - review & editing. Baojing Zhou: Conceptualization, Methodology, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111405.

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