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Bilayer MOF@MOF and MoO_x species functionalization to access prominent stability and selectivity in cascade-selective biphase catalysis

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ARTICLE INFO ABSTRACT Keywords: A novel bilayer metal-organic framework (viz., MOF@MOF, based on Zr-MOFs via epitaxial growth of UiO-bpy UiO-66@UiO-bpy on preformed UiO-66) assembled with two-dimensional MoO_x species was designed and synthesized. The MoO_x species MoO_x@UiO-66@MoO_x@UiO-bpy composite would improve substrates/products diffusion, avoid active metals Encapsulation leaching, and crucially provide a new platform via trapping intermediates and regulating the desired reaction Cascade-selective catalysis direction. As confirmed via characterization results, MoO_x@UiO-66@MoO_x@UiO-bpy with micro-/mesopores and strong acid sites (Lewis and Brønsted) exhibited good thermal and chemical stability. The bilayer MoO_x@UiO-66@MoO_x@UiO-bpy was further tested in cascade-selective biphase cyclopentene oxidation and exhibited 10.3% cyclopentene conversion and 16.9% glutaric acid selectivity higher than those of MoO_x@UiO-66, due to its large specific surface area, high content of MoO_x species, micro-/mesoporous structure, and bilayer catalytic effect. Its good reusability (> 10 runs) in the solvent-free-biphase cyclopentene oxidation suggested multidimensional encapsulation of active species in bilayer MOFs providing new idea for designing highselectivity/stability heterogeneous catalysts. Besides, a set of reaction kinetic models with detailed kinetic parameters and a detailed reaction mechanism were provided, reconfirming the key to develop the technology of

1. Introduction

Metal-organic frameworks (MOFs), an emerging family of organicinorganic hybrid materials, have aroused tremendous attention in academia and industry due to their potential capacity in catalysis [1,2], separation [3,4], gas storage [5,6], and carbon capture [7,8], *etc.*. Compared with other porous materials [9–11], MOFs provide greater structure versatility [12], facility to design [13], adjustable porosity [14], much higher surface area [15], and relatively effortless confinement of guest species [16]. These features permit MOFs acting as a novel type of platform to assemble bi-/multifunctional characteristics into one system for plentiful catalysis, especially for cascade catalysis [17–20]. Particularly, Zr-MOFs, assembled *via* linear dicarboxylate and Zr₆O₄(OH)₄(O₂CR)₁₂ units [21], have become attractive candidates for constructing novel catalytic materials due to their extraordinary thermal/chemical stability, low toxicity of Zr, as well as robust redox

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stability obtained *via* selecting chelating ligands with pyridyl moieties (*e.g.*, bipyridines, terpyridines, or phenanthrolines) [22,23].

cyclopentene to glutaric acid was to conquer cyclopentene oxide hydrolysis activation energies (E_2 and E_4). Compared to our previous study, E_2 and E_4 values were decreased 93.8 and 31.7 kJ·mol⁻¹, respectively.

Many efforts to the development of active species encapsulated MOFs (denoted as species@MOFs), for a large scale of catalysis system, were done [24]. The fascination depends on the variety of nearly unlimited combinations, referring to both employed MOFs and immobilized species. The frameworks of MOFs feature individual properties because of their variable metal clusters and the functional organic entities, whereas the confined species represent functional and catalytic sites [25]. Combination of both generates synergetic effects, beneficial to a large amount of application [26]. Nevertheless, the microporosity of the conventional MOFs may generally result in diffusion limitation of the anticipate catalytic transformation [27], and the leaching of metal particles during the reaction process is inevitable [28]. Accordingly, confining species in hollow MOFs composites has become possible which can accelerate an effective transport of reactants to the internal





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Fig. 1. XRD patterns (a) and BET isotherms (b, pore size distribution (inset)) of different materials.

surface with simultaneously improved desorption of products [29], but a continuous activity decrease because of the loss of active particles from open-ended pores is still a critical problem. The conventional MOFs are sometimes difficult to meet special needs leading to the emergence of hybrid or multifunctional MOFs composites [30,31]. Therefore, the so-called MOF@MOF with bilayer hetero-structure were developed via epitaxial growing another MOF on preformed MOF to bring changes in their physical/chemical properties compared with a single MOF material or intrigue unexpected synergies. Zhuang et.al [32] designed a fracture-free Pd-UiO-66@ZIF-8 MOF, which displayed excellent size-selective hydrogenation catalysis and high stability for prolonged reactions (17 h). Compared with UiO-67-BPY-Ag, UiO-66@UiO-67-B-PY-Ag showed a 22% improvement of 3-phenylpropiolic acid yield, and just < 0.0013% Ag was detected in the filtrate after a series cycles, suggesting the relatively better stability of UiO-66@UiO-67-BPY-Ag [33].

Obviously, selective oxidation of cyclopentene to glutaric acid with H₂O₂, an important green and efficient cascade-selective biphase oxidation, has been explored for many years [34-38], but there is no commercial installation so far. The fundamental reason is that it is difficult to coordinate and balance the catalytic activity, target product oriented selectivity, and catalyst stability, especially the poor directional selectivity is particularly unacceptable in cascade liquid catalysis. Homogeneous catalysts (tungstic acid or molybdophosphate heteropoly acid, etc.) with excellent catalytic activity always generate poor reusability and contamination via residual catalyst. Transition metal oxides of Mo, W, Fe, and Co have been confirmed serving as heterogeneous catalysts active sites for many reactions [38-42]. Among numerous heterogeneous catalysts, Mo/W-based catalysts have showed promising activity because of their oxidation potentials appropriate for actuating the oxidation reaction and multiple Lewis acidity sites [43-45]. Based on the above-mentioned description, it still remains an enormous challenge to design suitable Mo/W-based heterogeneous catalysts with superior directional selectivity to the target product while facilitating reactants/products diffusion and inhibiting leaching of active species for cyclopentene selective oxidation.

Herein, inspired *via* the double layers structure of kidney which has a porous cystic cavity structure facilitating the transport of H_2O and electrolyte and previous research work, we designed a hybrid metalorganic framework $MoO_x@UiO-66@MoO_x@UiO-bpy$ with bilayer structure all assembled with MoO_x species (active sites). In the solvent-free selective oxidation of cyclopentene with H_2O_2 , $MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-66@MoO_x@UiO-bpy exhibits three superior functions: 1) improving the transport of reactants and products due to the increased specific surface area and mesopores; 2) largely avoiding the leaching of active <math>MoO_x$ species owing to the confinement of bilayer structure; 3) crucially trapping intermediates and regulating the desired reaction direction with 92.5% selectivity to glutaric acid.

2. Experimental section

2.1. Catalysts synthesis

ZrCl₄ (99.5 wt%), 1,4-benzene dicarboxylic acid (99 wt%), glacial acetic acid (99.5 wt%), DMF (99.5 wt%), MeOH (99.5 wt%), 2,2'-bipyridine-5,5'-dicarboxylic acid (98 wt%), and $(NH_4)_6Mo_7O_{24}$ ·4H₂O (99 wt%) were purchased from Macklin Company. Cyclopentene (98 wt%) and H₂O₂ (35 wt%) were obtained from Kangderui Chemical Technology Co., Ltd.

2.1.1. UiO-66 and UiO-bpy

UiO-66 and UiO-bpy were synthesized on the basis of the reported literatures [28,46,47]. The detailed synthetic procedure was exhibited in Supporting Information.

2.1.2. MoO_x@UiO-66

UiO-66 (0.5 g) was added to $(NH_4)_6Mo_7O_{24}$ ·4H₂O aqueous solution (20 mg·mL⁻¹, 12 mL), and the mixture was stirred at 40 °C for 48 h to obtain a suspension solution. The resulting $MoO_x@UiO-66$ was collected, washed, purified, and dried with similar procedure as the preparation of UiO-66 or UiO-bpy, and calcined at 300 °C for 5 h.

2.1.3. MoO_x@UiO-66@UiO-bpy

ZrCl₄ (0.047 g, 0.2 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (0.049 g, 0.2 mmol), glacial acetic acid (0.4 mL), and DMF (30 mL) were placed in a 50 mL flask. The mixture was sonicated for 2 h before $MoO_x@UiO-66$ (0.1 g) introducing. Afterwards, the suspension solution was sonicated for another 40 min, and then transferred to Teflon-lined stainless steel autoclave (50 mL) and heated at 120 °C for 24 h. After cooling, sample was isolated and washed with DMF. After soaking with MeOH, the solid was dried at 100 °C overnight to obtain $MoO_x@UiO-66@UiO-bpy$.

2.1.4. MoO_x@UiO-66@MoO_x@UiO-bpy

The same synthetic procedure was employed as $MoO_x@UiO-66$ except that UiO-66 was replaced with $MoO_x@UiO-66@UiO-bpy$.

2.2. Characterization

Textural properties of the materials were measured via N_2 sorption at 77 K on a Micromeritics ASAP 2020 sorptometer. Powder X-ray diffraction (PXRD) was conducted on a Rint 2000 vertical goniometer with Cu K α radiation. Fourier-transform infrared spectroscopy (FT-IR) was performed on a Nicoet 460 from 4000-400 cm⁻¹. Thermogravimetric measurements (TG) were carried out on a STA 449C. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded on CARY 500 UV-VIS NIR spectrophotometer. Surface acidity was monitored from FT-IR spectra collected after pyridine adsorption.



Fig. 2. FT-IR (a) and UV-Vis DRS spectra (b) of related materials.



Fig. 3. TG curves (a) and Py-FT-IR spectra (b) of related materials.



Fig. 4. Cyclopentene oxidation catalyzed over different composites under optimized reaction conditions $(a, C_t/C_0 = \frac{n_t(cyclopentene)/V}{n_0(cyclopentene)/V})$ and hot filtration test (b).

Table 1	
Kinetic data $k_{1\sim 5}$ of cyclopentene oxidation with the two catalysts.	

Samples	$k (\text{L-mol}^{-1} \cdot \text{s}^{-1})$				
-	k_1	k_2	k_3	k_4	k_5
MoO _x @UiO-66 MoO _x @UiO- 66@MoO _x @UiO-bpy	6.8193 18.0305	0.5811 3.4952	4.6094 19.8143	1.7350 7.8111	10.9500 25.2519

2.3. Selective oxidation of cyclopentene

Cyclopentene selective oxidation was performed in a three-necked, round-bottomed flask provided with a condenser, a constant pressure dropping funnel, and a thermometer. Typically, cyclopentene (0.6813 g, 10 mmol) was added to the flask containing $MoO_x@UiO$ -

Tab	le 2	
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Kinetic data of	f cyclopentene	e oxidation w	ith MoO_@UiC	-66@MoO.	.@UiO-bpv.
					(C

$A (\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1})$		$E (kJ \cdot mol^{-1})$		
A1	2.48×10^8	E1	49.07	
A ₂	$9.66 imes 10^{14}$	E ₂	97.99	
A ₃	$1.34 imes10^7$	E ₃	39.42	
A ₄	$2.30 imes10^{16}$	E_4	105.55	
A ₅	$\textbf{2.01}\times \textbf{10}^{7}$	E ₅	40.06	

66@MoO_x@UiO-bpy (0.1 g). The mixture was stirred and the temperature was raised to 45~50 °C, then, H₂O₂ (35 wt%, 4.08 g, 42 mmol) was slowly added to the system. Samples were periodically extracted and analyzed *via* GC. After 3 h reaction, MoO_x@UiO-66@MoO_x@UiObpy was filtered hot and the reaction was permitted to continue without catalyst.



Fig. 5. Reusability test (a), XRD (b), and FT-IR (c) patterns of recovered MoO_x@UiO-66@MoO_x@UiO-bpy.



Scheme 1. Bilayer structure of $MoO_x@UiO-66@MoO_x@UiO-bpy$ in nature and by design. Left: multilayer structure of glomerulus, which own large surface area to enhance the exchange of H_2O and electrolyte. Right: bilayer structure of UiO-66@UiO-bpy assembly with MoO_x species.



Scheme 2. Synthetic strategy of UiO-66@UiO-bpy assembly with MoO_x species.

3. Results and discussion

Scheme 1 illustrates the bilayer structure of $MoO_x@UiO-66@MoO_x@UiO-bpy$ in nature and by design. Meanwhile, Scheme 2 depicts the strategy for synthesizing bilayer UiO-66@UiO-bpy composed of MoO_x species.

3.1. Catalyst characterization

Powder X-ray diffraction (XRD) studies (Fig. 1a) revealed the crystal structure of $MoO_x@UiO-66@MoO_x@UiO$ -bpy and related precursor materials. Patterns of both UiO-66 (layer B) and UiO-bpy (layer A)

closely matched the reported patterns [48]. After the loading of MoO_x species, the peak positions of $MoO_x@UiO-66$ were in line with UiO-66, suggesting UiO-66 frame structure was well-preserved. The same was true for $MoO_x@UiO-66@UiO-bpy$ and $MoO_x@UiO-66@MoO_x@-UiO-bpy$. Nevertheless, the peak intensities of UiO-66 were reduced, perhaps due to the slight change in framework structural regularity when the MoO_x species were deposited [49]. In comparison with $MoO_x@UiO-66@UiO-bpy$, the peak intensities of $MoO_x@-UiO-66@UiO-bpy$, the peak intensities of $MoO_x@-UiO-66@MoO_x@-UiO-66@UiO-bpy$ peak intensities of crystallinity, suggesting that $MoO_x@UiO-66@UiO-bpy$ peak intensities decreased after the introduction of MoO_x species. In addition, no characteristic peaks of MoO_x were detected in the diffraction patterns of



Scheme 3. Cascade-selective cyclopentene oxidation over MoO_x@UiO-66@MoO_x@UiO-bpy.

 $MoO_x@UiO-66@UiO-bpy$ and $MoO_x@UiO-66@MoO_x@UiO-bpy$, implying that MoO_x species were highly dispersed or/and the loading of MoO_x species content was too low to generate a signal. Generally, each XRD peak of $MoO_x@UiO-66@MoO_x@UiO-bpy$ could be attributed to either UiO-66 or UiO-bpy, while some were a result of peak overlap. The well-defined peaks suggested the decent crystallinity of $MoO_x@$ -UiO-66@MoO_x@UiO-bpy, UiO-66, as well as UiO-bpy.

 N_2 sorption data were recorded at 77 K. The BET isotherms exhibited the porosity of these composites, as a type I sorption isotherms were observed (Fig. 1b). The surface area of UiO-66, $MoO_x@UiO-66$, $MoO_x@UiO-66@UiO-bpy$, and $MoO_x@UiO-66@MoO_x@UiO-bpy$ were 892, 619, 1121, 935 m²·g⁻¹, respectively. The smaller surface area of $MoO_x@UiO-66$ and $MoO_x@UiO-66@MoO_x@UiO-bpy$ over related precursor materials (UiO-66 and $MoO_x@UiO-66@UiO-bpy$, respectively) was contributed to the additional introduction of MoO_x species. Nevertheless, the surface area improved greatly after the epitaxial growth of UiO-bpy layer. The growth of UiO-bpy could improve $MoO_x@UiO-66$ porosity resulting in increased surface area. Comparison of the pore distribution curves (Fig. 1b, inset) revealed that $MoO_x@UiO-66@MoO_x@UiO-bpy$ possessed an extended porosity in mesopores region, distinctly indicating that the epitaxial growth of UiO-bpy layer enhanced the mesoporosity. These results evidenced that UiO-66@UiO-bpy owned multimodal porosities and larger surface area, which were significant for mass transfer of reactants and products.

Fig. 2a depicted the FT-IR spectra of different composites. The spectra of $MoO_x@UiO-66$ not only had typical infrared bands assigning to UiO-66, but also contained typical infrared bands attributing to MoO_x species, revealing that MoO_x structure maintained intact even when confined in UiO-66 pores. Furthermore, there were characteristic bands of MoO_x , UiO-66, and UiO-bpy in the vibrational spectra of $MoO_x@UiO-66@UiO-bpy$ and $MoO_x@UiO-66@MoO_x@UiO-bpy$. Nevertheless, the characteristic bands of MoO_x intensity became stronger, owing to the



Scheme 4. Cyclopentene oxidation over $MoO_x@UiO-66@MoO_x@UiO-bpy$ with H_2O_2 .

secondary encapsulation of MoO_x contents [50]. Besides, the change on color, from pale yellow to yellow, offered an evidence of the encapsulation (Fig. S1a, Supporting Information). After the multidimensional confinement of MoO_x species, the color of the corresponding catalyst was obviously deepened. In order to further confirm the existing of MoO_x species in UiO-66@UiO-bpy, the EDS mapping of C, O, Zr, and Mo elements (Fig. S1b, Supporting Information) that displayed uniform distribution of MoO_x in $MoO_x@UiO-66$ and $MoO_x@UiO-66@$

MoO_x@UiO-bpy, and the Energy Dispersive Spectrometer (EDS) analysis of MoO_x@UiO-66 and MoO_x@UiO-66@MoO_x@UiO-bpy were also measured (Fig. S1c, Supporting Information). Besides, the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) manifested the Mo contents were 2.49 wt% *versus* 4.93 wt%, respectively. The solid state UV-Vis DRS spectra of related composites were depicted in Fig. 2b. MoO_x@UiO-66 exhibited an absorption peak at *ca.* 295 nm due to the ligand to metal charge transfer O^{2−} → Mo⁶⁺ [38]. Impressively,



Scheme 5. Circulation of cyclopentene distillate.

 $MoO_x@UiO-66@UiO$ -bpy showed a large red shift of 310 nm compared to $MoO_x@UiO-66$, and a peak located at *ca*. 375 nm attributed to UiO-bpy was observed [51] indicating the successful epitaxial growth of UiO-bpy on UiO-66. An intense absorption peak (*i.e.*, 310 nm) for $MoO_x@UiO-66@MoO_x@UiO$ -bpy was assigned to the secondary MoO_x species confinement, corresponding to the color change from pale yellow for $MoO_x@UiO-66$ or $MoO_x@UiO-66@UiO$ -bpy to yellow for $MoO_x@UiO-66@MoO_x@UiO$ -bpy.

Thermal stability of different composites were investigated via thermogravimetric analysis (TG, Fig. 3a), and the results both exhibited high thermal stability (up to 450 °C) of MoO_x@UiO-66@MoO_x@UiO-bpy and suggested that the successful epitaxial growth of UiO-bpy and encapsulated MoO_x species. The mass loss of MoO_x@UiO-66@MoO_x@UiO-bpy at 450~550 °C was higher than that of MoO_x@UiO-66@UiO-bpy and MoO_x@UiO-66 owing to the secondary encapsulation of MoO_x species and the epitaxial growth of UiO-bpy, respectively. Pyridine adsorption measured via IR spectroscopy was carried out to estimate the types and strength of acid sites of MoO_x@UiO-66@MoO_x@UiO-bpy. Fig. 3b exhibited the FT-IR spectra recorded after pyridine adsorption and subsequent evacuation at 40, 120, and 350 °C. The Pv-FT-IR spectrum recorded at 40 °C on $MoO_r@UiO-66@MoO_r@UiO-bpy$ revealed bands at 1444 and 1604 cm⁻¹, assigned to pyridine coordinately bonded to weak surface Lewis (viz., L) acid sites, which maintained almost entirely after outgassing at 120 °C. Besides, the spectra recorded displayed bands at 1492, 1549, and 1641 cm⁻¹ because of protonated pyridine bonded to surface Brønsted (i.e., B) acid sites. The intensity of these bands reduced after outgassing with increasing temperature, but they were still existed even after outgassing at 350 °C, indicating that L and B acid sites were rather strong, and the relative amount of L, B, and total acidity was listed (Table S1, Supporting Information). Based on Py-FT-IR, it can be concluded that both L and B acid sites were evidenced over MoOx@UiO-66@MoOx@UiO-bpy and that the strong L and B acid sites were essential to cyclopentene selective oxidation [52].

These characterization results depicted that UiO-66@UiO-bpy was formed in the existence of MoO_x and MoO_x had been *in situ* confined in the micro- and mesopores of UiO-66@UiO-bpy. That is, the $MoO_x@UiO-66@MoO_x@UiO-bpy$ composite where MoO_x species uniformly distributed within the framework of UiO-66@UiO-bpy has been synthesized and fully characterized.

3.2. Catalytic tests

 $MoO_x@UiO-66@MoO_x@UiO-bpy$ catalytic performance was evaluated in cyclopentene oxidation employing H_2O_2 as an oxidant without any solvent. In order to investigate the optimal reaction conditions, the related experiments were based on an orthogonal design (L25 matrix, Table S2, Supporting Information).

Fig. 4a compared catalytic activity under optimized reaction conditions obtained *via* range analysis over $MoO_x@UiO-66$, $MoO_x@UiO-66@MoO_x@UiO-bpy$, UiO-66@UiO-bpy, and commercial MoO_3 as a benchmark, and the corresponding cyclopentene conversion data was also listed. As exhibited in Fig. 4a, there was significant difference in the catalytic performance. The higher catalytic activity of the bilayer $MoO_x@UiO-66@MoO_x@UiO-bpy$ with $C_t/C_0 = 75.3\%$ (*viz.*, 24.7% cyclopentene conversion) and 92.5% glutaric acid selectivity was assigned to the more active MoO_x content (4.93 wt% *versus* 2.49 wt%), the enhanced diffusion of substrates/products obtained by multimodal porosities containing micro-/mesopores and the larger internal surface (935 *versus* 619 m²·g⁻¹), and the platform provided *via* bilayer structure to capture the intermediates and convert them to the target product. Compared with high glutaric acid selectivity (92.5%), the relative low cyclopentene conversion (24.7%) was assigned to the mass transfer resistance existed between the oil and H₂O phases.

To quantitatively compare the catalytic activity of $MoO_x@UiO-66$ and $MoO_x@UiO-66@MoO_x@UiO-bpy$, the reaction rate constants ($k_{1\sim5}$, Table 1, Scheme 3) were calculated *via* adopting the established reaction models [2].

Apparent rate constants $k_{1\sim5}$ were determined to be 6.8193 *versus* 18.0305, 0.5811 *versus* 3.4952, 4.6094 *versus* 19.8143, 1.7350 *versus* 7.8111, 10.9500 *versus* 25.2519 L·mol⁻¹·s⁻¹ for MoO_x@UiO-66 *versus* MoO_x@UiO-66@MoO_x@UiO-bpy, indicating the reaction was easier to occur when MoO_x@UiO-66@MoO_x@UiO-bpy was employed as the catalyst. The reaction rate constants $k_{1\sim5}$ for cyclopentene oxidation over MoO_x@UiO-66@MoO_x@UiO-bpy were also investigated at different temperatures (70, 85, and 90 °C, Table S3, Supporting Information) to calculate the activation energy.

According to Arrhenius equations ((1)~(2), Where *A*, *E*, *R*, and *T* are *pre*-exponential factor, activation energy, gas constant, and absolute temperature, respectively), ln*k versus* $1000 \cdot T^{-1}$ plots (Fig. S2, Supporting Information) provided the corresponding activation energy values (Table 2).

$$k = Ae^{-(E/RT)} \tag{1}$$

$$\ln k = \ln A - \frac{E}{RT}$$
(2)

The conclusion suggested that the key to develop the technology of **A** to **F** was to overcome the activation energies (E_2 and E_4) of **D** hydrolyzation, and this was consistent with our previous research. Nevertheless, the lower E_2 (97.99 (this work) *versus* 191.82 kJ·mol⁻¹ [2]) and E_4 (105.55 (this work) *versus* 137.29 kJ·mol⁻¹ [2]) for MoO_x@-UiO-66@MoO_x@UiO-bpy acted as catalyst might be due to its larger surface area and multimodal porosities (micro- and mesopores), which were beneficial to the transfer and diffusion of the molecules.

Since MoO_x species were confined in double layers, their leaching was distinctly suppressed, which was confirmed *via* hot filtration test in cyclopentene oxidation reaction. $MoO_x@UiO-66@MoO_x@UiO-bpy$ was separated from the reaction system *via* centrifugation after 3 h and the resulting filtration was continued reacted at 85 °C for another 5 h (Fig. 4b). No distinct reduction of C_t/C_0 was detected after the separation of catalyst (a slight decrease assigned to the fraction that was thermodynamically converted even without catalyst). According to the above results and previous studies [2,53,54], we reasoned that such an efficient performance was owing to the unique feature of $MoO_x@UiO-66@MoO_x@UiO-bpy$ for mediating the cascade-selective reaction, and for the first time, the detailed reaction mechanism was proposed (Scheme 4).

As exhibited in Scheme 4, in layer A, H_2O_2 molecules might first attack MOO_x species and coordinate with Mo center to generate Mo-OOH (**b**), subsequently, Mo-OOH radical (**c**) reacted with C=C of cyclopentene to generate the important intermediate product **D**. On the one hand, under the action of **b** and H_2O , the ring of **D** opened to form 2hydroperoxycyclohexanol (**1**), which was rearranged to **E**. Glutaraldehyde radical (**2**) reacted with H_2O_2 and **E** producing glutaraldehyde peroxyacid (**3**) which could be further reacted with **E** to (**4**). Aldehydic acid (**5**) was formed *via* the rearranged of **4**, and **5** continued to be oxidized into **F**. On the other hand, **D** hydrolyzed to give **G**, which was transformed to cyclopentanone (**6**) with the existence of H^+ . **6** underwent Baeyer-Villiger oxidation reaction producing valerolactone (**7**), which further converted to 5-hydroxypentanoic acid (**8**) *via* hydrolyzation. Subsequently, 8 was oxidized to 5, and finally 5 was further oxidized to F.

Based on the catalytic performance, we presumed that the abovementioned reaction process reoccurred in layer B, causing A and the intermediate products (**D**, **E**, and **G**) further converted into **F**, thereby high **F** selectivity exhibited. Nevertheless, due to the existence of mass transfer resistance between the oil and H₂O phases, unsatisfactory **A** conversion showed.

3.3. Catalyst reusability

Fig. 5a depicted that $MoO_x@UiO-66@MoO_x@UiO-bpy$ maintained ~75.71% C_t/C_0 (*i.e.*, ~24.3% cyclopentene conversion) and ~91.2% glutaric acid selectivity in the 10 repeated uses, and when the reaction completely finished, the metal leaching in the reaction solution were 0.009, 0.005, 0.004, 0.004, 0.003, 0.003, 0.001, 0.0013, 0.001, 0.001 wt% for each of 10 repeated cycles, respectively. Additionally, the metal leaching (0.475 wt%) of $MoO_x@UiO-66$ was also detected after the first run. Compared to $MoO_x@UiO-66$, the metal leaching was decreased *via* more than one order of magnitude which was a significant improvement of the catalyst reusability. What's more important, trace leaching of Mo was beneficial to glutaric acid purification, and the colorless glutaric acid crystals was obtained through the process depicted in Scheme S1 (Supporting Information).

To further explore the stability of the composite, $MoO_x@UiO-66@MoO_x@UiO-bpy$ recovered from the reaction system was characterized *via* XRD and FT-IR. The XRD spectra (Fig. 5b) of $MoO_x@UiO-66@MoO_x@UiO-bpy$ remained unchanged after the 10th catalytic run, implying the $MoO_x@UiO-66@MoO_x@UiO-bpy$ material contained a highly stable structure in cyclopentene oxidation system, which was in line with the results of FT-IR (Fig. 5c).

3.4. Material circulation

During the purification process of **F** (Scheme S1, Supporting Information), the distillate **A** was employed as circulated material to perform the oxidation reaction again (Scheme 5), which was beneficial to the environment and the commercialization of **F**. The use of H_2O_2 , solvent-free, and cyclopentene circulation made the selective oxidation of cyclopentene reaction a truly green process.

4. Conclusions

A novel material $MoO_x@UiO-66@MoO_x@UiO-bpy$ was successfully synthesized *via* multidimensional MoO_x confined in UiO-66@UiO-bpy and employed as heterogeneous catalyst in cascade-selective cyclopentene reaction, which was reusable over at least 10 repeated runs without significant losing in catalytic activity. Besides, a set of reaction kinetic models with detailed kinetic parameters and a detailed reaction mechanism were proposed. The synergetic design of multidimensional MoO_x species within the bilayer structure evidenced that excellent target product selectivity could be obtained *via* double-layer catalytic and offered open mind of forming high-performance heterogeneous catalysts. The reaction system established with solvent-free, splendid target product selectivity, low activation energy, and substrate circulation system promoted the development of green catalytic oxidation technology for olefins.

CRediT authorship contribution statement

Qingtao Niu: Conceptualization, Methodology, Investigation, Funding acquisition. Manman Jin: Formal analysis, Project administration, Funding acquisition, Resources. Guodong Liu: Methodology, Software, Validation. Zhiguo Lv: Formal analysis, Funding acquisition. Chongdian Si: Funding acquisition, Visualization. Hong Han: Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2021.111818.

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