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Introduction

Biomass as one kind of practical and sustainable carbon source has been regarded as a very promising alternative resource to fossil fuels to produce valuable chemicals.^{1–3} 5-Hydroxymethylfurfural (HMF), which is primarily obtained from biomass by dehydration of fructose, is an ideal intermediate for synthesis of various chemicals *via* different catalytic routes. The selective catalytic oxidation of HMF is an effective pathway to produce several kinds of furan compounds, such as 2,5-diformylfuran (DFF), 5-formyl-2furancarboxylic (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 2,5-furandicarboxylic acid (FDCA).⁴ Among them, DFF has attracted much attention recently due to its potential application in the preparation of polymers,⁵ heterocyclic ligands,⁶ organic conductors,⁷ and pharmaceuticals.⁸

DFF is generated through partial oxidation of the hydroxymethyl group in HMF without disturbing the more reactive



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In this study, α -MoO₃ nanobelts were successfully synthesized by a simple, green and economic hydrothermal method and applied as a bifunctional catalyst for one-step conversion of fructose to DFF under atmospheric air. The structure of the as-prepared α -MoO₃ catalyst was characterized in detail by SEM, TEM, EDS, XRD, XPS, H₂-TPR and NH₃-TPD to better understand the relationship between structure and performance. α -MoO₃ nanobelts exhibited high catalytic activities for production of DFF from HMF and fructose in atmospheric air. Under optimized reaction conditions, high DFF yields of 97.2% and 78.3% were obtained by using HMF and fructose as raw materials, respectively. Furthermore, a plausible reaction pathway was proposed for the selective oxidation of HMF to DFF according to the experimental and catalyst characterization results. Importantly, α -MoO₃ is a robust catalyst that can be used at least five times without obvious loss in its catalytic activity. In brief, α -MoO₃ is an easily-prepared, eco-friendly, low cost and highly effective catalyst which has potential application in one-step conversion of fructose to DFF under atmospheric air.

α,β-unsaturated aldehyde group, which encounters a challenge. Many traditional oxidants including BaMnO₄,⁹ NaOCl,¹⁰ 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)¹¹ and pyridinium chlorochromate (PCC)¹² have been investigated for selective oxidation of HMF to DFF. However, these oxidation processes suffer from low atomic utilization, equipment corrosion and separation difficulties. In recent years, molecular oxygen as a green oxidant has been intensively used for preparation of DFF from HMF in various heterogenous catalytic systems. Among them, Mn-,¹³⁻¹⁶ Co-,^{17,18} V-,^{19,20} and Ru-^{21,22} based metal/metal oxide catalysts and non-metal carbon-based catalysts^{23,24} enable high activity and selectivity for aerobic oxidation of HMF to DFF. However, the large-scale production of DFF from HMF is still limited by the high cost of HMF, which is typically obtained by acid-catalyzed dehydration of fructose.

To reduce the production cost of DFF, integration of fructose dehydration with HMF oxidation in a one-pot reaction has attracted much attention and become a research hotspot. Combined use of an acid and a redox catalyst by stepwise addition is a feasible strategy for one-pot conversion of fructose to DFF. Many effective catalyst couples have been reported, such as Amberlyst-15 and Ru/HT,²⁵ Fe₃O₄-SBA-SO₃H and K-OMS-2,²⁶ Fe₃O₄-RGO-SO₃H and ZnFe_{1.65}Ru_{0.35}O₄,²⁷ and dilute sulfuric acid and V₂O₅/ceramic.²⁸ Another feasible strategy is using a bifunctional catalyst which possesses both acidity and oxidizability. 3D flower-like micro/nano Ce–Mo composite



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Paper

oxides $(f-Ce_{10-x}Mo_xO_\delta)$,²⁹ MoO₃-containing protonated nitrogen doped carbon (Mo-HNC),³⁰ sulfonated MoO₃-ZrO₂,³¹ V-g-C₃N₄ (H^+) ³² Vanadium-embedded mesoporous carbon microspheres (V-CS),³³ graphene oxide,³⁴ bifunctional carbon nanoplatelets³⁵ and others³⁶⁻³⁸ have been prepared and applied in the one-pot synthesis of DFF from fructose. However, complicated experimental operations were needed to achieve a high DFF yield in both combined catalyst systems and bifunctional catalyst systems. The fructose dehydration reaction was first proceeded in a N2 atmosphere to avoid the direct oxidation of fructose. After fructose was completely converted to HMF, the N₂ atmosphere was switched to an O₂ atmosphere to trigger an HMF oxidation reaction. The reported catalytic systems which need switching of inert gas is not a real one-step method. Additionally, in the existing catalytic systems for DFF preparation, pure O₂ which was stored in a high-pressure cylinder was used as an oxidant, giving high requirements for equipment and may cause security issues.

For large-scale production, economical, eco-friendly and easy to operate properties should also be emphasized while pursuing efficiency in direct conversion of fructose to DFF. Atmospheric air, which is an easily available, safe and economic O2 source, is more attractive for use as an oxidant for catalytic oxidation reactions. From this perspective, a bifunctional catalyst which can catalyze the reaction of HMF oxidation to DFF without disturbing the -OH groups in the structure of fructose under atmospheric air will be very attractive. MoO₃ which is of great interest for catalytic, optical and electrochemical applications³⁹⁻⁴¹ is found as thus an attractive bifunctional catalyst in this paper. Firstly, we successfully synthesized α -MoO₃ nanobelts by a simple, green and economic hydrothermal method. Then, systematic experiments proved that α-MoO₃ showed excellent catalytic performance for direct conversion of fructose to DFF under atmospheric air. The yield of DFF was up to 78.3% under the optimized reaction conditions.

Experimental

Materials

5-Hydroxymethylfurfural (HMF) was purchased from Beijing HWRK Chem Co. Ltd. Fructose, sodium molybdate dehydrate, perchloric acid, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), toluene, *p*-chlorotoluene, methyl isobutyl keton (MIBK), CH₃CN and H₂SO₄ were purchased from Sinopharm Chemical Reagent Co. Ltd. Naphthalene, MnO₂, Mn₂O₃, VO₂ and RuO₂ was purchased from Aladdin Reagent Co., Ltd. DFF was purchased from TCI (Shanghai) Development Co. Ltd. All reagents were used without further purification.

Preparation of α -MoO₃ nanobelts

 α -MoO₃ nanobelts was easily prepared according to previous literature.⁴² In a typical procedure, 16 mL of perchloric acid solution (4 mol L⁻¹) was added slowly into 10 mL of sodium molybdate solution (0.2 mol L⁻¹) under constant stirring. After thoroughly mixing, the mixture was moved into a hydrothermal

reactor and kept at 140 $^\circ C$ for 24 h. After cooling down to room temperature, the product was filtered, washed several times with ethanol and then vacuum dried at 80 $^\circ C$ overnight.

Catalyst characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed using an S-4800 microscope (HITACHI; Japan). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed using a JEM-2100F (JEOL; Japan) operated at 200 kV. The X-ray diffraction (XRD) spectrum was obtained using a Rigaku D/Max-2500 X-ray diffractometer (Rigaku; Japan) with Cu Ka radiation. The X-ray photoelectron spectroscopy (XPS) data was collected using a PHI-5000 versa probe (Ulvac-Phi; Japan) with Al Ka radiation. The temperature programmed desorption (TPD) of NH₃ was performed on a Micromeritics 2920 Autochem II Chemisorption Analyzer under a 5% NH₃/Ar gas flow (50 mL min⁻¹) at a rate of 5 $^{\circ}$ C min⁻¹ up to 550 $^{\circ}$ C. The temperature programmed reduction (TPR) of H₂ was performed on a chemisorption analyzer under a 2% H₂/Ar gas flow (30 mL min⁻¹) at a rate of 5 $^{\circ}$ C min⁻¹ up to 900 $^{\circ}$ C.

Catalytic oxidation of HMF to DFF

In a typical procedure, HMF (126 mg, 1 mmol), α -MoO₃ (50 mg) and DMSO (2 mL) were added into a glass tube. The reaction was performed under atmospheric air and maintained at the reaction temperature for a specific time under vigorous stirring. Finally, the reaction was quickly terminated by cooling the reactor to room temperature in an ice bath, and the sample was taken from the mixture for product analysis.

One-step conversion of fructose to DFF

In a typical procedure, fructose (180 mg), α -MoO₃ (50 mg), and DMSO (2 mL) were added into a glass tube. The reaction was performed under atmospheric air and maintained at the reaction temperature for a specific time under vigorous stirring. Finally, the reaction was quickly terminated by cooling the reactor to room temperature in an ice bath, and the sample was taken from the mixture for product analysis.

Recycling and leaching tests

In a typical procedure, after being separated from the reaction mixture by filtration, α -MoO₃ was washed with H₂O and alcohol several times and dried at 80 °C overnight. Then, α -MoO₃ was reused for the next cycle under the optimum reaction conditions. The possibility for Mo leaching during the oxidation reaction was tested as follows. After the oxidation of HMF catalyzed by α -MoO₃ proceeded under optimum reaction conditions for 2 h, the reactor was cooled down to room temperature by quenching with an ice bath. Then, the catalyst was filtered using a 0.22 µm filter, and the filtrate was reheated to 120 °C for another 6 h.

Analytical method

After the reaction, the mixture was diluted to 100 mL with deionized water and filtered using PTFF filters (0.22 $\mu m).$ The

liquid products were analyzed by HPLC (Agilent 1260 Infinity) with an instrument equipped with a refractive index (RI) detector and Aminex HPx-87H Ion Exclusion column (7.8 mm \times 300 mm) using dilute H₂SO₄ solution (0.004 M) as the eluent at a flow rate of 0.6 mL min⁻¹. The fructose conversion, HMF, DFF and FFCA yields were calculated on the basis of external standard curves constructed with authentic standards.

Results and discussion

Catalyst characterization

The crystal structure of the as-synthesized powder sample was characterized using an XRD technique. As shown in Fig. 1, the strong diffraction peaks at $2\theta = 12.85^{\circ}$, 23.47° , 25.9° , 27.41° , 33.74° , 35.58° , 39.12° , 45.9° , 46.45° and 49.34° are indexed as the (020), (110), (040), (021), (111), (041), (060), (200), (210) and (002) crystal planes of the orthorhombic MoO₃ phase (commonly denoted as α -MoO₃, JCPDS No. 05-0508). The absence of noticeable impurity peaks suggests the high purity of the α -MoO₃ product. The strong intensity of the reflection peaks of (020), (040) and (060) indicated the anisotropic growth of the α -MoO₃.

The SEM and TEM images (Fig. 2a and b) showed the α -MoO₃ sample as an entirely belt-like structure with a width of about 40 to 100 nm, and length of about several microns. The HRTEM image (Fig. 2c) of an individual nanobelt provided further insight into the structure of the nanomaterial, and some short-range ordering of oxygen vacancies could be found. The SAED pattern (Fig. 2d) recorded perpendicular to the growth axis of the single nanobelt could be attributed to the [010] zone axis diffraction of α -MoO₃, and suggested that the nanobelt grew along the [001] direction with the TEM information. We used SAED to characterize different parts of the same nanobelt, as well as different nanobelts. All electron diffraction patterns indicated almost the same [001] orientation of the nanobelt, implying that the α -MoO₃ nanobelts are wellcrystallized single crystallites. The EDS quantitative analysis showed the only existence of Mo and O elements, with a molar ratio close to 1:3 (Fig. S1, ESI⁺).



Fig. 1 XRD pattern of the as-synthesized α-MoO₃.



Fig. 2 (a) SEM, (b) TEM, (c) HRTEM and (d) SAED images of the asprepared $\alpha\text{-MoO}_3.$

H₂-TPR was performed to better understand the redox property of α-MoO₃ and the result is presented in Fig. 3a. Two intense peaks are observed obviously over the temperature range 570–760 °C and >760 °C. The first peak is attributed to the reduction of Mo⁶⁺ to Mo⁴⁺, which consists of the reduction of small crystalline MoO₃ (570–670 °C) and the reduction of bulk crystalline MoO₃ (670–760 °C). The second peak located at higher temperature (>760 °C) is assigned to the reduction of Mo⁴⁺ to Mo^{0.43} The good reducibility of α-MoO₃ may be in favour of the redox process in the conversion of HMF to DFF.

Surface acid sites are crucial to the dehydration of fructose to HMF. NH_3 -TPD was performed to study the surface acid sites of α -MoO₃ and the result is shown in Fig. 3b. A broad peak was



Fig. 3 (a) H_2 -TPR curve and (b) NH_3 -TPD curve of α -MoO₃.

Comparison of different metal oxides for catalyzed oxidation of HMF to DFF

The as-prepared α -MoO₃ and several common metal oxides were first used as catalysts for the HMF oxidation reaction under atmospheric air, and the results are summarized in Table 1. As expected, negligible HMF conversion and DFF yield were obtained in the absence of catalyst (Table 1, entry 1). With α -MoO₃ is used as a catalyst, 100% conversion of HMF with 97.2% yield of DFF was achieved (Table 1, entry 2). Other metal oxides including MnO2, Mn2O3, V2O5 and RuO2 have been reported as highy effective catalysts for selective oxidation of HMF to DFF by using oxygen as the oxidant.^{44,45} However, only moderate HMF conversions (27.8-47.3%) and DFF yields (18.5-42.2%) were obtained in the catalysis of these metal oxides under atmosphere air (Table 1, entries 3-6). In the above HMF oxidation reactions, FFCA was detected as the only by-product. The experimental results indicated that the as-prepared α -MoO₃ showed the highest catalytic activity for selective oxidation of HMF to DFF under atmospheric air among the metal oxides screened.

Process parameter optimization for catalytic oxidation of HMF to DFF by $\alpha\text{-}MoO_3$

Solvent has a crucial effect on the HMF oxidation reaction. As shown in Table 2, strongly polar and high-boiling solvents, including DMSO and DMF, are desirable reaction media for selective oxidation of HMF to DFF catalyzed by α -MoO₃. High DFF yields (97.2% and 95.8%, respectively) and selectivities (both 100%) were obtained in DMSO and DMF (Table 2, entries 1 and 2). Low-boiling aromatic solvents, such as toluene and p-chlorotoluene, have been reported as good solvents for HMF oxidation to DFF. However, in this study, toluene and *p*-chlorotoluene only give moderate activities of α -MoO₃ with HMF conversions of 76.5% and 80.4%, and DFF yields of 70.0% and 75.2%, respectively (Table 2, entries 3 and 4). Other common low-boiling solvents, including MIBK, CH₃CN and H₂O were also used, giving low HMF conversions and DFF yields (Table 2, entries 5–7). With toluene, p-chlorotoluene, MIBK, CH₃CN and H₂O as solvents, other oxidation products including FDCA and FFCA were detected as by-products. From

Table 1	Catalytic oxidation of HMF to DFF by different metal oxides						
	Catalyst	Conversion (%)	DFF yield (%)	Selectivity (%)			
Entry				DFF	FFCA		
1	_	5.0	2.5	50	0		
2	MoO_3	100	97.2	97.2	2.8		
3	MnO_2	30.2	23.6	78.1	3.2		
4	Mn_2O_3	27.4	18.5	67.5	1.6		
5	VO ₂	47.3	42.2	89.2	5.5		

Reaction conditions: HMF 0.126 g (1 mmol), catalyst 50 mg, DMSO 2 mL, 120 $^\circ \! \mathrm{C},$ 8 h.

36.2

80.8

3.5

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Table 2 The oxidation of HMF to DFF in different solvents

				Selectivity (%)					
Entry	Solvent	Conversion (%)	DFF yield (%)	DFF	FFCA				
1	DMSO	100	97.2	97.2	2.8				
2	DMF	100	95.8	95.8	4.2				
3	Toluene	76.5	70.0	91.5	8.0				
4	<i>p</i> -Chlorotoluene	80.4	75.2	93.5	6.2				
5	MIBK	55.2	42.3	76.6	20.2				
6	CH ₃ CN	30.5	14.2	46.5	50.3				
7	H_2O	24.1	10.4	43.2	55.5				
Reaction conditions: HMF 0.126 g (1 mmol), α -MoO ₃ 50 mg, solvent 2 mL, 120 °C, 8 h.									

the experimental results, DMSO and DMF offered a desirable HMF conversion as well as DFF selectivity, probably owing to the high stability of both HMF and DFF, as well as improved dissolution of O_2 in these solvents.

Then, the effects of reaction time, temperature and amount of catalyst on the α-MoO3-catalyzed oxidation of HMF to DFF were studied. From Fig. 4a, both HMF conversion and DFF yield increased gradually with the reaction time in the initial stage, reaching the highest at 8 h. Further prolonging the reaction time to 10 h, the yield of DFF had a minute decrease, because DFF continued to be oxidated to FFCA and FDCA. The selectivity of DFF decreased gradually with passage of reaction time, but still was up to 97% at 8 h, which is the most suitable reaction time for α -MoO₃-catalyzed oxidation of HMF to DFF. From Fig. 4b, the conversion of HMF and the yield of DFF increased gradually as the reaction temperature increased from 90 to 120 °C. Further increasing the reaction temperature to 130 °C, the yield of DFF decreased from 97% to 95%. Furthermore, the selectivity of DFF decreased gradually with the reaction temperature increasing from 80 to 130 °C, probably due to high temperature favouring the conversion of DFF to FFCA. From Fig. 4c, HMF conversion and DFF yield increased gradually with catalyst amount increase from 10 mg to 50 mg, and reached the highest at 50 mg under the same reaction conditions. The results indicate that there are not enough active sites for complete HMF conversion when the amount of catalyst is less than 50 mg. Moreover, insufficient catalyst loading (10 mg and 20 mg) resulted in a little lower DFF selectivity. This may be due to the formation of other insoluble by-products such as humins, as no FFCA or FDCA was detected.

Leaching tests and recyclability

The long-term stability of a catalyst is one of the most important merits of heterogeneous catalysts. The possibility for Mo leaching during the oxidation reaction was tested as follows. After the oxidation of HMF catalyzed by α -MoO₃ proceeded under optimum reaction conditions for 2 h, the reactor was cooled down to room temperature by quenching with an ice bath. Then, the catalyst was filtered using a 0.22 µm filter, and the filtrate was reheated to 120 °C for another 6 h. From Fig. S2 (ESI†), the yield of DFF has no obvious change after removing the catalyst. Moreover, the reaction mixture was collected and analyzed by ICP-OES. The concentration of molybdenum ion in

RuO₂

44.8

6



Fig. 4 Effects of (a) reaction time, (b) temperature and (c) amount of catalyst on α -MoO₃-catalyzed oxidation of HMF to DFF. If not specified, the default reaction conditions are as follows: HMF 126 mg, α -MoO₃ 50 mg, DMSO 2 mL, temperature 120 °C and reaction time 8 h.

the reaction mixture was measured as only 15.8 ppm, which means that the leaching of molybdenum ion from the catalyst is negligible during the reaction. The reusability of α-MoO₃ was also examined for selective oxidation of HMF to DFF. The solid catalyst was recovered by centrifugation, washed thoroughly with water and ethanol, dried in an oven and then recycled for the next reaction. As shown in Fig. 5, α -MoO₃ could be reused for at least five runs without obvious deactivation. HMF conversion and DFF yield both only decreased slightly after five funs. Interestingly, the DFF selectivity almost keeps constant with the recycling of α -MoO₃. The TOF values in the five recycling experiments were calculated as 0.86, 0.86, 0.84, 0.82 and 0.81 respectively. Additionally, SEM and EDS were used to analyse the morphology and composition of the recycled catalyst which had been used five times. As shown in Fig. S3 (ESI⁺), the morphology and composition of the recycled catalyst both have no obvious change. The above results demonstrate the high stability of α -MoO₃ during HMF oxidation to DFF.



Fig. 5 Recycled experiments at the optimal conditions for the oxidation of HMF to DFF catalyzed by α -MoO₃. Reaction conditions: HMF 0.126 g (1 mmol), α -MoO₃ 50 mg, DMSO 2 mL, 120 °C, 8 h.

Reaction mechanism of HMF oxidation over α-MoO₃

To discuss the reaction mechanism of HMF oxidation to DFF over α -MoO₃, the structure of fresh α -MoO₃, α -MoO₃ used under atmospheric air (α -MoO₃-air) and α -MoO₃ used under N₂ atmosphere (α -MoO₃-N₂) were analyzed by XPS. From Fig. 6a, the O 1s spectrum of the fresh α -MoO₃ can be deconvoluted into two peaks, which are assigned to the surface lattice oxygen (symbolized as O_{α}) with relatively low binding energies around 529–530 eV and other oxygen species (symbolized as O_{β}) with binding energies around 531–531 eV, respectively. From Table S1 (ESI†), compared to the fresh α -MoO₃, α -MoO₃-air shows a



Fig. 6 The XPS spectra of (a) O 1s and (b) Mo 3d of α -MoO₃.

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lower ratio of $O_{\alpha}/(O_{\alpha} + O_{\beta})$. Furthermore, when the reaction was performed in a N_2 atmosphere, the ratio of $O_{\alpha}/(O_{\alpha} + O_{\beta})$ decreased obviously further after the reaction. From Fig. 6b, in the Mo 3d spectrum of the fresh catalyst, the two peaks at 233 and 236 eV corresponding to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ respectively, suggest that the composition of the as-prepared catalyst is MoO₃, which is in accordance with the EDS result. Compared to the fresh α -MoO₃, there are two other small peaks at 231.2 and 234.4 eV in the Mo 3d spectrum of α -MoO₃-air, indicating that a tiny amount of Mo with a lower oxidation state (between VI and IV) was formed. Similarly, a higher ratio of Mo^{\delta}+/Mo⁶⁺ (4 < δ < 6) is obtained after the reaction performed under a N₂ atmosphere.

From the XPS results, under atmospheric air, the ratio of O_{α} / $(O_{\alpha} + O_{\beta})$ was slightly decreased in the O1s spectra, indicating that lattice O²⁻ was consumed after the reaction. When the HMF oxidation reaction was performed under a N₂ atmosphere, the content of lattice O2- decreased more obviously. These results illustrate that the consumed lattice O²⁻ on the surface of α -MoO₃ can be replenished in the presence of atmospheric air. However, the recovery rate of active lattice O^{2-} species is lower that the consumption of them as the ratio of $O_{\alpha}/(O_{\alpha} + O_{\beta})$ on the surface of α -MoO₃-air is decreased. Moreover, the increased content of O_{β} is indirect proof of the increased content of oxygen vacancies, and the Mo^{δ^+} is relevant to the creation of oxygen vacancies. In the Mo 3d XPS spectra, the appearance of Mo^{δ^+} on the surface of α -MoO₃-air indicates that more oxygen vacancies appear on α -MoO₃-air. The similar increasing trend in the content of lattice O^{2-} and Mo^{δ^+} on the surface of used α -MoO₃ (in air and N₂) identifies that the lattice O²⁻ species is closely associated with the redox potential of α -MoO₃. According to the XPS analysis results, the lattice O²⁻ species serves as the active sites in the HMF oxidation reaction. The reaction undergoes the following pathways according to the Mars-van-Krevelen mechanism. In Scheme 1, the hydroxymethyl species of HMF were firstly adsorbed on the surface of α -MoO₃ and then the lattice O²⁻ species were consumed to



Scheme 1 Possible reaction mechanism for α -MoO₃-catalyzed oxidation of HMF to DFF under atmospheric air.



Fig. 7 One-step synthesis of DFF from fructose catalyzed by α -MoO₃ under atmospheric air. Reaction conditions: fructose 0.18 g (1 mmol), α -MoO₃ 50 mg, DMSO 2 mL, 120 °C.

form DFF along with the reduction of Mo^{6+} to $Mo^{\delta+}$. Finally, the $Mo^{\delta+}$ was reoxidized by the chemisorbed molecular oxygen, which continuously supplied the active lattice O^{2-} species *via* the cyclic redox couple of Mo^{6+} and $Mo^{\delta+}$ ions.

One-step synthesis of DFF from fructose catalyzed by α -MoO₃ under atmospheric air

From an economical viewpoint, fructose is a more attractive raw material to prepare DFF via acid-catalyzed dehydration and selective oxidation by a one-step method. Considering the excellent acidity and oxidizability of α -MoO₃, we attempted the synthesis of DFF directly from fructose under atmospheric air. Firstly, fructose was used as the raw material to produce HMF and DFF in the catalysis of α -MoO₃ under different reaction temperature and time to obtain the highest carbon balance. The results are shown in Fig. S4 (ESI[†]), the highest carbon balance was calculated as 83% which was obtained at 120 °C for 2 h. Then, the reaction time was prolonged to achieve the highest yield of DFF. As shown in Fig. 7, both HMF and DFF were detected at the initial reaction time. The intermediate product HMF attained a maximum yield of 56.1% in 1 h and received full conversion in 8 h. The yield of DFF increased gradually with reaction time, reaching the highest of 78.3% in 8 h. After the reaction, the reaction mixture was heavily coloured, indicating the formation of humins in the fructose dehydration step. The selectivity of DFF in the HMF oxidation step is calculated as 94.3% according to the carbon balance in 2 h (83%) and the yield of DFF in 8 h (78.3%), which is a little lower than that obtained by using HMF as the raw reactant (97.2%). The reason for this smay be that a little amount of HMF or DFF was adsorbed on the surface of the formed humins.

Conclusions

 α -MoO₃ nanobelts were successfully synthesized by a simple hydrothermal method. The characterization results reveal that the α -MoO₃ nanobelts are well-crystallized single crystallites,

possess medium acid sites and have good reducibility which may favor the one-step reaction of fructose to DFF. Then, α -MoO₃ was applied as a bifunctional catalyst for DFF production under atmospheric air. Under optimum reaction conditions, high DFF yields of 97.2% and 78.3% were obtained by using HMF and fructose as reactants, respectively. Furthermore, a plausible reaction pathway was proposed for α -MoO₃-catalyzed oxidation of HMF to DFF based on the experimental and catalyst characterization results. The lattice O^{2-} on α -MoO₃ serves as the active sites to realize the oxidation of the hydroxy group in HMF. The consumption of the lattice O^{2-} on α -MoO₃ is replenished by the chemisorbed molecular oxygen during the reaction and then α -MoO₃ is involved in the next catalytic cycle process. Additionally, the α -MoO₃ nanobelts exhibited high stability and could be used at least five times without obvious loss in their catalytic activity. In brief, α-MoO₃ is an easilyprepared, eco-friendly, low cost and highly efficienct catalyst for one-step conversion of fructose to DFF under atmospheric air.

Conflicts of interest

There are no conflicts to declare.

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