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Aerobic oxidation of biomass derived 5-hydroxymethylfurfural into 5-hydroxymethyl-2-furancarboxylic acid catalyzed by a montmorillonite K-10 clay immobilized molybdenum acetylacetonate complex

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In this study, we have successfully prepared a heterogeneous catalyst (K-10 clay-Mo) by the immobilization of bis(acetylacetonato) dioxo-molybdenum(VI) [$MoO_2(acac)_2$] on montmorillonite K-10 clay. The structure of the resultant catalyst was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electronic microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy. The catalytic activity of K-10 clay-Mo was tested in the aerobic oxidation of 5-hydroxymethylfurfural (HMF). Although a molecule of HMF contains one hydroxyl group and one aldehyde group, to our surprise, the catalyst showed high catalytic activity for the oxidation of the aldehyde group of HMF into 5-hydroxymethyl-2-furancarboxylic acid (HMFCA). A variety of important reaction parameters such as the reaction temperature, catalyst amount, and solvent were explored. HMFCA could be obtained in a high yield of 86.9% with a HMF conversion of 100% after a short reaction time of 3 h in toluene. More importantly, the catalyst K-10 clay-Mo could be reused several times without a significant loss of its catalytic activity.

Introduction

At present, we are entering an epoch of diminishing availability of petrochemical resources, which are mainly used to produce chemical products and energy for our society.[1] In order to reduce the dependence on fossil fuels, it is worthwhile to develop new routes to effectively convert renewable resources into fuels and chemicals.[2] Unlike other renewable resources, biomass is the only widely available carbon source apart from fossil resources. Therefore, only biomass resources can contribute to the promising development of effective methods for the production of fuels and chemicals from renewable resources.[3] In recent years, an enormous effort has been devoted to the development of effective methods for the production of fuels and chemicals from biomass.[4]

One of the most attractive directions in biorefinery is devoted to the production of furan derivatives, such as furfural and 5-hydroxymethylfurfural (HMF).[5] HMF, which is the acidic-catalyzed dehydration product of C6 based carbohydrates, is widely considered as a versatile platform chemical, and it can be used as a sustainable precursor for the preparation of a broad range of chemicals and liquid transportation fuels.[6] In this context, the synthesis of HMF has been extensively studied in various catalytic systems from edible biomass.[7] The oxidation of HMF can generate several kinds of furan compounds such as 2,5-furandicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF). FDCA and DFF have been regarded as a promising monomer for the synthesis of furan-containing polymers and fine chemicals.[8] In recent years, there is an overwhelming research on the synthesis of FDCA and DFF from the oxidation of HMF.[9] The oxidation of the aldehyde group in HMF can produce another important oxidation product HMFCA. HMFCA serves not only as a monomer in the synthesis of various polyesters,[10] but also shows antitumor activity[11] and is a promising building block of an interleukin inhibitor.[12] Unlike the research interest towards the synthesis of FDCA and DFF, the synthesis of HMFCA from the oxidation of HMF has remained limited. The reason for this might be due to the selective oxidation of the aldehyde group into a carboxylic group, leaving the hydroxyl group intact. As shown in Scheme 1, the oxidation of HMF can generate various oxidation products including 5-formyl-2-furancarboxylic acid (FFCA), HMFCA, DFF and FDCA. There are few reports on the synthesis of HMF into HMFCA. Mitsukura *et al.*, developed a method for the synthesis of HMFCA by the

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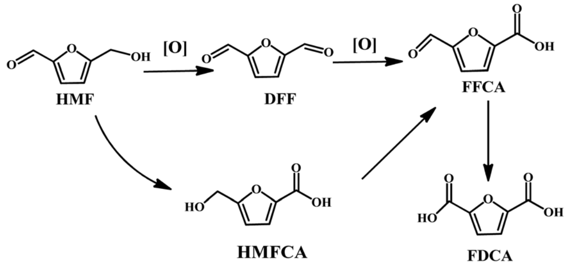

Scheme 1 Schematic illustration of the oxidation products during the oxidation process of HMF.

biocatalytic oxidation method using whole cells LF14 as the catalyst.[13] Recently, the classic Cannizzaro reaction has also been used for the synthesis of HMFCA.[14] The Cannizzaro reaction produced a low HMFCA yield, and a high concentration of alkaline waste. Recently, supported noble metals have been designed for the synthesis of HMFCA from the aerobic oxidation of HMF.[15] Some of them require a high oxygen pressure or NaOH. For example, Davis *et al.*,[15a] have prepared supported gold for the oxidation of HMF , achieving a HMFCA yield of up to 90% at 690 kPa O_2 in 0.3 M NaOH. Therefore, the development of synthetic strategies for the effective synthesis of HMFCA from HMF is a challenging and promising area in biorefinery.

Montmorillonite K-10 clay is a type of acidic stratified silicate mineral with a three-layer structure,[16] which is commercially available with a low cost. These interlayer cations of the K-10 clay can undergo exchange with various cations from external solutions. Therefore, the K-10 clay has been considered as a promising support for the immobilization of homogeneous complexes to construct various heterogeneous catalysts.[17] At present, dioxomolybdenum(VI) complexes are reported to show high catalytic activity for alkene epoxidation using environmentally benign oxidants such as hydrogen peroxide and alkyl hydroperoxides.[18,19] However, the studies on the oxidation of alcohols with dioxomolybdenum(VI) complexes as catalysts are still very limited.[20] In 2012, Gao *et al.*, prepared a new heterogeneous dioxo-molybdenum(VI) complex, by the reaction of $MoO_2(acac)_2$ with aldehyde group-modified crosslinked polystyrene (CPS) microspheres, and found that this catalyst showed the ability to activate molecular oxygen for the oxidation of benzyl alcohols to benzaldehyde.[20b]

Herein, inspired by the high cation-exchange capacity of K-10 clay and the ability of dioxomolybdenum(VI) complexes in the activation of molecular oxygen, a heterogeneous catalyst was prepared by the immobilization of $MoO_2(acac)_2$ on K-10 clay. The prepared catalyst showed high catalytic activity for the oxidation of HMF into HMFCA with molecular oxygen.

Experimental section

Materials and method

$MoO_2(acac)_2$ was purchased from Aladdin Chemicals Co. Ltd (Shanghai, China). 5-Hydroxymethylfurfural (98%) was supplied by Beijing Chemicals Co. Ltd (Beijing, China). 5-Hydroxymethyl-2-furancarboxylic acid (98%) was purchased from J & K Co. Ltd (Beijing, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). Montmorillonite K-10 clay was purchased from Ziyi Chemicals Co. Ltd (Shanghai, China), and the chemical composition (average value) was as follows: SiO_2 (73.0%), Al_2O_3 (14.0%), Fe_2O_3 (2.7%), CaO (0.2%), MgO (1.1%), Na_2O (0.6%), K_2O (1.9%). All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and were freshly distilled before use.

Catalyst preparation

The catalyst was prepared by the immobilization of the $MoO_2(acac)_2$ complex on the K-10 clay (abbreviated as K-10 clay-Mo). Typically, prior to use, the K-10 clay was dried at 110 °C for 3 h to remove adsorbed water. $MoO_2(acac)_2$ (0.6325 g) was firstly dissolved in 50 mL of dry toluene with magnetic stirring. Then the K-10 clay (1.0 g) was added and the mixture continuously stirred at room temperature for 24 h. After reaction, the K-10 clay-Mo catalyst was obtained by filtration and thoroughly washed with hot ethanol several times to remove any unreacted metal complex. Finally, the K-10 clay-Mo catalyst was dried at 110 °C for 5 h.

Catalyst characterization

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G^2-20 instrument. The sample powder was firstly dispersed in ethanol and dropped onto a copper grid for observation. FT-IR measurements were recorded on a Nicolet NEXUS-6700 FTIR spectrometer with a spectral resolution of 4 cm^{-1} in the wave number range of 500–4000 cm^{-1}. The X-ray powder diffraction (XRD) patterns of the samples were determined with a Bruker advanced D8 powder diffractometer (Cu Kα). All XRD patterns were collected in the 2θ range of 10–80° with a scanning rate of 0.016° s^{-1}. X-Ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at a constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected with referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard.

Procedures for the determination of Mo content by ICP-AES

The molybdenum content in the K-10 clay-Mo catalyst was quantitatively determined by an inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The acid digestion was composed of concentrated HNO_3 (7.5 mL), 48 wt% HF (1.5 mL) and 2.5 mL concentrated HCl (2.5 mL). 0.5 g of the sample was digested in the above acid digestion solution on a flat electric furnace. After digestion, the sample was made up to 25 mL with deionized water and centrifuged at 3000 rpm. The supernatant liquid was taken for ICP-AES analysis. The ICP-AES operation conditions were as follows: incident power: 1.1 kW, carrier gas flow rate: 0.8 L min^{-1}, auxiliary gas flow rate: 0.4 L min^{-1}, coolant gas flow rate: 16 L min^{-1}, observation height: 10 mm.

General procedure for the aerobic oxidation of HMF to HMFCA

The aerobic oxidation of HMF was carried out in a 25 mL round bottom flask, which was equipped with a reflux condenser and capped with a balloon. Typically, HMF (1 mmol, 126 mg) was firstly dissolved into toluene (8 mL) with stirring. The K-10 clay-Mo catalyst was then added to the reaction mixture, and the vessel flushed with oxygen at a rate of 20 mL min^{-1} from the bottom of the reactor, and the reaction was carried out at 110 °C at a constant stirring rate of 600 revolutions per minute (rpm) to exclude the effect of the stirring rate on the reaction. Time zero was recorded when oxygen was flushed into the reaction mixture. After reaction, the K-10 clay-Mo catalyst was removed from the reaction mixture and the products were analyzed by HPLC.

Identification and quantification of the products

^{1}H NMR and ^{13}C NMR spectra were conducted on a Bruker DRX-400 spectrometer at 298 K. An Agilent 6890 network GC/5973 MS equipped with a HP-5 silica capillary column, size 30 m × 0.25 mm was used to determine molecular weights of the final products.

Quantification of HMF and HFMCA were performed on a HPLC device using an external standard calibration curve method. Samples were separated by a reversed-phase C18 column (200 × 4.6 mm) at a wavelength of 280 nm. Acetonitrile and 0.1 wt% acetic acid aqueous solution (v : v = 30 : 70) were used as the mobile phase with a flow rate of 1.0 mL min^{-1}. The column temperature was maintained at 30 °C. Standard curves for HMF and HFMCA were then constructed so that the concentration of HMF and HFMCA in the samples could be determined.

To calculate the conversion of HMF eqn (1) was used.

$$\text{HMF conversion} = \text{moles of converted HMF}/\text{moles of starting HMF} \times 100\% \tag{1}$$

One molecule of HMF gave rise to one molecule HMFCA, thus the yield of HMFCA can be calculated using eqn (2).

$$\text{HMFCA yield} = \text{moles of HMFCA}/\text{moles of starting HMF} \times 100\% \tag{2}$$

Results and discussion

Characterization of K-10 clay-Mo

Firstly, the ICP/AES determination showed that the weight percentage of the Mo element in the K-10 clay-Mo catalyst was 0.98 wt%. The XRD patterns of the K-10 clay support and the K-10 clay-Mo catalyst are shown in Fig. 1. The K-10 clay shows a crystalline structure. It is not difficult to distinguish several broad 2θ peaks located at about 20, 35, 54 and 62°, which are assigned to the diffractions of the (110), (105), (210) and (300) reflections, respectively.[21] In addition, a sharp peak at 2θ = 26.5 belongs to quartz.[22] On comparison of the XRD pattern of the K-10 clay with that of the K-10 clay-Mo, there is no difference between them, which indicated that the clay structure is retained after the immobilization of $MoO_2(acac)_2$. This situation is consistent with the previous report in the literature for Mn(III) salen complexes immobilized between the clay layers of K-10 clay.[23] In addition, it was reported that $MoO_2(acac)_2$ has its own characteristic XRD peaks with JCPDS card (00-022-1833). Therefore, we have mechanically mixed $MoO_2(acac)_2$ with K 10 clay and achieved a Mo content of up to 0.98%, and analyzed the XRD patterns. There was also no XRD peaks for $MoO_2(acac)_2$. Thus, the main reason for the disappearance of $MoO_2(acac)_2$ in the K-10 clay-Mo catalyst was due to the low content of the Mo.

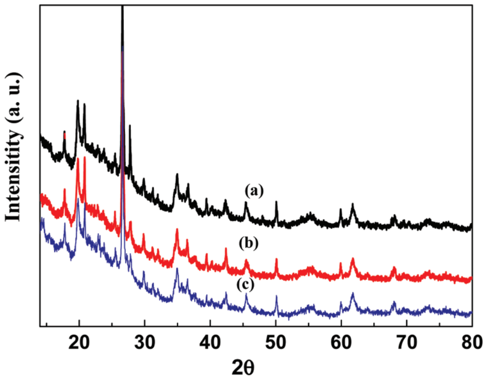

Fig. 1 XRD patterns of the samples. (a) K-10 clay; (b) K-10 clay-Mo; (c) the mechanical mixing of the two solids [$MoO_2(acac)_2$ and K-10 clay].

The valence state of the Mo element in the K-10 clay-Mo catalyst was characterized by XPS technology. The measurement was carried out with reference to the C 1s binding energy (284.6 eV) as an internal standard. The survey scan of the Mo 3d region is shown in Fig. 2. It shows Mo 3d lines at 232.4 eV

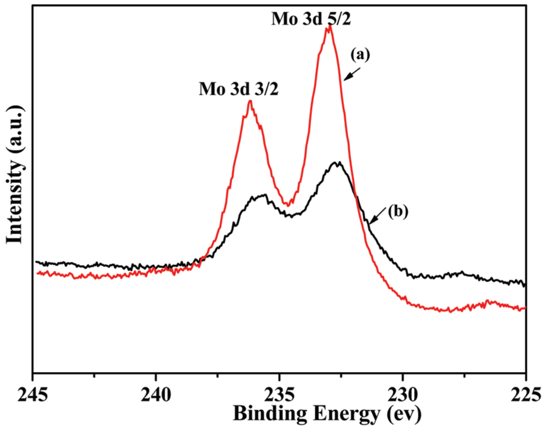

Fig. 2 XPS spectra of the samples (a) the mechanical mixing of the two solids [$MoO_2(acac)_2$ and K-10 clay]; (b) the catalyst K-10 clay-Mo.

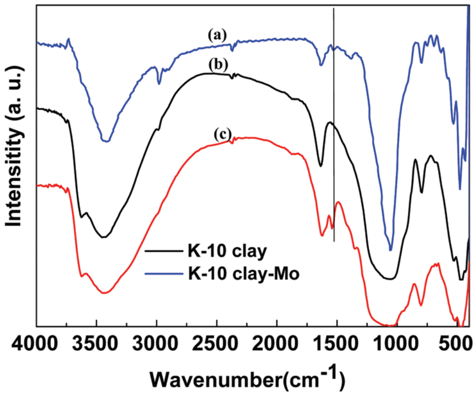

Fig. 3 FT-IR spectra of spectra of the samples. (a) The mechanical mixing of the two solids [$MoO_2(acac)_2$ and K-10 clay]; (b) K-10 clay; (c) K-10 clay-Mo.

(3d5/2) and 235.5 eV (3d3/2), which is characteristic of molybdenum metal in the +6 oxidation state.[24] In order to obtain deeper insights into the structure of the catalyst, the mechanical mixing of the two solids [$MoO_2(acac)_2$ and K-10 clay] was also analyzed by the XPS technology. As shown in Fig. 2, it was found that the peaks of Mo 3d5/2 and 3d3/2 were shifted to a higher binding energy region, which corresponded to 233.0 eV and 236.1 eV, respectively. The values were derived from the free $MoO_2(acac)_2$. The slight difference of the XPS results between K-10 clay-Mo and the mixture of the two solids [$MoO_2(acac)_2$ and K-10 clay] indicated that $MoO_2(acac)_2$ was chemically bond on the support K-10 clay.

Before the characterization of FT-IR, the samples were heated at 120 °C in vacuum oven overnight to release any physisorbed H_2O, thus it can exclude the effect of water on the FT-IR spectra. The strong and wide bands at 3400 cm^{-1} were present in the FT-IR spectra of all the samples (Fig. 3), and it should be attributed to the structural-OH stretching vibration[25] and the band at 1630 cm^{-1} is related to OH deformation.[26] In the low energy region, an intense and broad band over the range of 1000–1200 cm^{-1} is observed in both the spectra of the K-10 clay and K-10 clay-Mo catalyst, which is attributed to the Si–O stretching vibrations of the tetrahedral layer. After immobilization of $MoO_2(acac)_2$ on the K-10 clay support two bands appeared at 905 and 950 cm^{-1}, although the two bands were not distinct. The two bands can be attributed to the terminal Mo=O stretching modes.[18] In addition, a band at 1537 cm^{-1} appeared for the K-10 clay-Mo catalyst, which corresponds to the vibration of the C=O group of acac.[19] In order gain further insight into the structure of the catalyst, the FT-IR spectrum of the mechanical mixing of the two solids [$MoO_2(acac)_2$ and K-10 clay] with a Mo content up to 0.98% was obtained, and it was found that the FT-IR spectrum of the K-10 clay-Mo catalyst was almost the same as that of the mechanical mixing of two solids [$MoO_2(acac)_2$ and K-10 clay]. However, there was a shift of the C=O stretching vibration. The band was at 1532 cm^{-1} in the mechanical mixture of the two solids, which was derived from the free $MoO_2(acac)_2$, whereas it was 1537 cm^{-1} for the K-10 clay-Mo catalyst. There results once again verified that $MoO_2(acac)_2$ was supported on the K-10 clay support through chemical bonds.

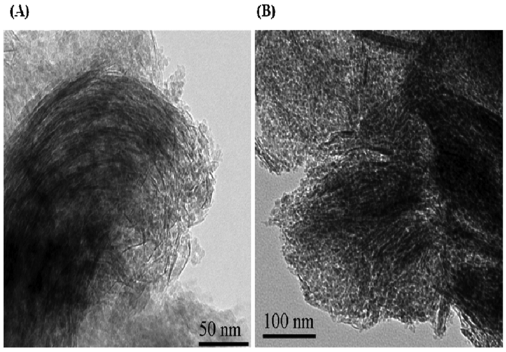

Fig. 4 TEM images of the samples. (A) K-10 clay; (B) K-10 clay-Mo.

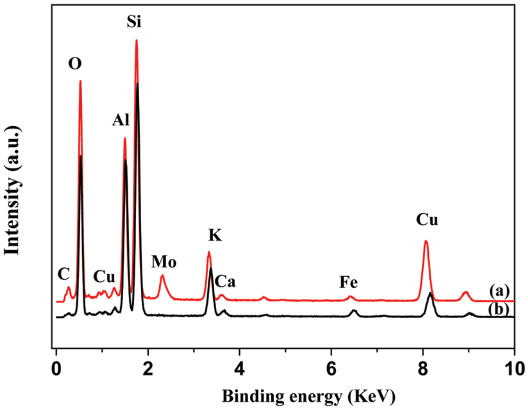

Fig. 5 The energy-dispersive analysis of X-ray (EDAX) of the samples. (a) K-10 clay-Mo; (b) K-10 clay.

TEM images of the K-10 clay and K-10 clay-Mo catalyst are shown in Fig. 4. It reveals that the K-10 clay support presents a multilayer structure. After the immobilization of $MoO_2(acac)_2$ on the K-10 clay support, it is clearly observed that the multilayer structure is maintained in the K-10 clay-Mo catalyst, but the TEM image of K-10 clay-Mo catalyst shows much darker regions. Furthermore, the K-10 clay and K-10 clay-Mo catalyst were further characterized by energy-dispersive analysis of X-ray (EDAX). As shown in Fig. 5, Mo was only presented in the K-10 clay-Mo catalyst, indicating that $MoO_2(acac)_2$ was successfully immobilized on the K-10 clay support. In addition, we also found that the content of Mo in the dark region (1.86%) was higher than that in the other parts (0.51%). These results indicated that the distribution of Mo varied over the K-10 clay material. Our results were consistent with those reported by Farias *et al.*[27]

The aerobic oxidation of HMF into HMFCA under various conditions

Prior to testing the catalytic activity of the K-10 clay-Mo catalyst on the aerobic oxidation of HMF, the stability of HMF was

Table 1 Conversion of HMF into HMFCA under various conditions[a]

Entry	Catalyst	Catalyst amount (mg)	Time (h)	HMF con. (%)	HMFCA yield (%)
1[b]	—	—	2	0.3 ± 0.1	0 ± 0
2	—	—	2	0.7 ± 0.2	0 ± 0
3	K-10 clay	150	2	42.5	35.3
4	$MoO_2(acac)_2$	59	2	26.7	23.4
5	K-10 clay-Mo	150	2	92.5 ± 0.5	81.9 ± 0.4

[a] Reaction conditions: HMF (70 mg) and a set amount of catalyst were added to toluene (7 mL), and the reaction was carried out at 110 °C with the flushing of oxygen at a speed of 20 mL min^{-1}. [b] The reaction was carried out without catalyst and oxygen.

Table 2 The results of the aerobic oxidation of HMF into HMFCA in different solvents[a]

Entry	Solvent	HMF Con.[b] (%)	HMFCA yield (%)	HMFCA Sel.[c] (%)
1	DMSO	7.9 ± 0.4	7.2 ± 0.5	91.4
2	DMF	7.1 ± 0.3	6.8 ± 0.4	91.2
3	*p*-Chlorotoluene	90.3 ± 0.7	80.9 ± 0.5	89.6
4	Toluene	92.5 ± 0.5	81.9 ± 0.4	88.5
5	Trifluorotoluene	89.2 ± 0.6	82.6 ± 0.7	92.6
6	Acetonitrile	7.0 ± 0.4	6.2 ± 0.4	88.6
7	MIBK	31.0 ± 0.7	26.2 ± 0.6	84.5
8[d]	MIBK	96.6 ± 0.9	80.6 ± 0.8	83.4
9	Ethanol	65.9 ± 0.7	3.0 ± 0.5	4.5

[a] Reaction conditions: HMF (70 mg) and K-10 clay-Mo (150 mg) were added to organic solvent (7 mL), and the reaction was carried out at 110 °C for 2 h with the flushing of oxygen at a speed of 20 mL min^{-1}. [b] Con. is the abbreviation of conversion. [c] The selectivity (Sel.) was calculated by the use of the average values of HMF conversion and HMFCA yield. [d] The reaction time was 8 h.

studied. Although it has always been reported that HMF is not stable under acidic or alkaline conditions,[28] it was observed that HMF was stable in toluene with a recovery of 99.7% after 2 h at 110 °C (Table 1, entry 1). In addition, HMF also showed high stability even with the flushing of oxygen (Table 1, entry 2). Control experiments were also carried out using the K-10 clay support and $MoO_2(acac)_2$ as the catalysts, respectively. A HMFCA yield of 35.3% with a HMF conversion of 42.5% were obtained after 2 h in the presence of the K-10 clay (Table 1, entry 3). Further prolonging the reaction time to 12 h meant that the HMF conversion could reach 97.8% in the presence of K-10 clay, with a HMFCA yield of 72.1% after 12 h. These results indicated that the K-10 clay had the ability to catalyze the aerobic oxidation of HMF. Our results were consistent with the results reported by Dintzner *et al.*, in which they reported that montmorillonite KSF clay could catalyze the air oxidation of aliphatic aldehydes to the corresponding carboxylic acids.[29] As the composition of montmorillonite K-10 clay is complex, including SiO_2 (73.0%), Al_2O_3 (14.0%), Fe_2O_3 (2.7%), CaO (0.2%), MgO (1.1%), Na_2O (0.6%), K_2O (1.9%), some metal elements or metal oxides should be responsible for the catalytic ability in the oxidation reactions. For example, Zhu *et al.*[30] reported that Fe_2O_3 supported on carbon nitride could activate molecular oxygen.

Under the same reaction conditions, a HMF conversion of 26.7% and HFMCA yield of 23.4% were obtained after 2 h using $MoO_2(acac)_2$ as the catalyst (Table 1, entry 4). By further increasing the reaction time to 12 h the HMF conversion reached 57.8% and the yield of HMFCA was 38.5%. However, the K-10 clay-Mo catalyst showed a higher catalytic activity. A high HMFCA yield of 81.9% was obtained with a HMF conversion of 92.5% after 2 h when the reaction was conducted at 110 °C in the presence of the K-10 clay-Mo catalyst (Table 1, entry 5). On assessment of the results given in Table 1 (entries 3–5), the K-10 clay and Mo demonstrated an ability for the aerobic oxidation of HMF into HMFCA, however, they also demonstrated a synergetic effect on the promotion of the aerobic oxidation of HMF into HMFCA.

Effect of solvent on the aerobic oxidation of HMF into HMFCA

To study of the solvent effect on the catalytic activity of the K-10 clay-Mo catalyst, the aerobic oxidation of HMF was carried out in a variety of organic solvents under idenitcal conditions. As shown in Table 2, the solvent showed a remarkable effect on the HMF conversion and HMFCA yield. Low HMF conversions were obtained when the reactions were carried out in DMSO and DMF with strong polarities and high boiling points (Table 2, entries 1 & 2). Among the various solvents, aromatic solvents were found to be the best for the transformation. Similar HMF conversions around 90% and HFMCA yields around 81% were achieved after 2 h when the reactions were carried out in *p*-chlorotoluene, toluene and trifluorotoluene (Table 2, entries 3–5). Both the HMF conversion and HMFCA yield were low when the reaction was performed with acetonitrile as the solvent (Table 2, entry 6). When the reaction was performed in methyl isobutyl ketone (MIBK), HMFCA was obtained in a yield of 26.2% with a HMF conversion of 31.0% after 2 h at 110 °C (Table 2, entry 7). A high HMFCA yield of 80.6% could be obtained in MIBK after a long reaction time of 8 h (Table 2, entry 8). The good results demonstrated the possibility of synthesizing HMFCA from fructose through two steps. The first step involves the biphasic system (MIBK-water) for the production of HMF from fructose, in which the dehydration of fructose into HMF was performed in the water phase, and the product was extracted into the organic MIBK phase. Then the HMF in MIBK can be oxidized into HMFCA in the second step. A HMF conversion of 65.9% was obtained in ethanol, but HMFCA was only obtained in a low yield of 3.0% (Table 2, entry 9). 5-Ethoxymethylfurfural (EMF) was detected as the main product with a yield of 61.5%, which was produced by the acid-catalyzed etherification of the hydroxyl group in HMF with ethanol. The reason for this is that the K-10 clay is an acidic material, which is consistent with our previous results on the synthesis of EMF.[31]

Effect of reaction temperature and catalyst amount on the aerobic oxidation of HMF

With the aim of obtaining the optimal reaction conditions for the aerobic oxidation of HMF into HMFCA, the effect of the

Table 3 The effect of reaction temperature and catalyst amount on the aerobic oxidation of HMF[a]

Entry	Catalyst amount (mg)	T (°C)	Time (h)	HMF Con. (%)	HMFCA yield (%)
1	150	110	2	92.5 ± 0.5	81.9 ± 0.4
2	150	110	3	100 ± 0	86.9 ± 0.8
3	150	110	12	100 ± 0	85.4 ± 0.6
4	150	80	3	23.5 ± 0.6	22.5 ± 0.8
5	150	50	3	14.3 ± 0.5	13.4 ± 0.7
6	100	110	2	81.5 ± 0.9	71.9 ± 0.7
7	50	110	2	64.7 ± 0.5	57.2 ± 0.6
8	25	110	2	30.5 ± 0.4	26.8 ± 0.6
9	12.5	110	2	17.4 ± 0.7	15.3 ± 0.7
10	12.5	110	16	98.7 ± 0.3	84.7 ± 0.8

[a] Reaction conditions: HMF (70 mg) and a set amount of catalyst were added to toluene (7 mL), and the reaction was carried out at different reaction temperatures with the flushing of oxygen at a speed of 20 mL min^{-1}.

Table 4 Catalytic oxidation of HMF using various oxidants[a]

Entry	Oxidant	T (°C)	Time (h)	HMF Con. (%)	HMFCA yield (%)
1[b]	*t*-BuOOH	80	2	100 ± 0	0
2[b]	H_2O_2	80	2	5.2 ± 0.6	4.7 ± 0.5
3[c]	O_2	110	3	100 ± 0	86.9 ± 0.8
4[d]	O_2	110	2	75.2 ± 0.4	67.4 ± 0.6
5[d]	O_2	110	4	100 ± 0	86.1 ± 0.5
6[e]	Air	110	2	64.6 ± 0.6	58.5 ± 0.4
7[e]	Air	110	8	100 ± 0	83.6 ± 0.7

[a] Reaction conditions: HMF (126 mg, 1 mmol), K-10 clay-Mo (150 mg), and toluene (7 mL). [b] 7 mmol *t*-BuOOH or H_2O_2 were used. [c] With flushing of oxygen at a rate of 20 mL min^{-1}. [d] An O_2 balloon was employed. [e] In an air atmosphere.

main reaction parameters such as reaction temperature and catalyst loading were studied. It was noted that the effect of the reaction temperature was much more obvious than that of the catalyst loading. The higher the reaction temperature, the higher the HMFCA yield. It only took 3 h to obtain complete HMF conversion and the highest HMFCA yield of 86.9%, with the turnover number (TON) calculated to be 31.5 (Table 3, entry 2). Interestingly, it was found that HMFCA was stable at 110 °C without further oxidation to other products (Table 3, entry 3). The HMF conversion and HMFCA yield decreased sharply when the reaction temperature decreased from 110 °C to 80 °C and 50 °C. The observed HMF conversions were found to be 23.5% and 14.3% after the 3 h at the reaction temperature of 80 °C and 50 °C, respectively, which gave the corresponding DFF yields of 23.5% and 14.3%, respectively (Table 3, entries 4 and 5).

The effect of the catalyst amount on the aerobic oxidation of HMF into HMFCA was also studied. As shown in Table 3, the HMF conversion and HMFCA yield decreased with the decrease of the catalyst amount (Table 3, entries 1, 6–9). The increased HMF conversion and HMFCA yield with the increase of catalyst loading at an early reaction stage can be attributed to an increase in the availability and number of catalytically active sites for the aerobic oxidation of HMF. It was noted that a high HMF conversion of 98.7% and HMFCA yield of 84.7% were also obtained after 16 h, when 12.5 mg of the K-10 clay-Mo catalyst was used, with a low mole ratio of Mo to HMF being 0.24%. In addition, we have tried to increase the content of the substrate HMF, and found that the maximum HMF concentration in toluene was 23 mg mL^{-1} at the reaction temperature of 110 °C. Therefore, we have carried out the aerobic oxidation of HMF with 160 mg in 7 mL with 150 mg of catalyst at 110 °C, and we found that the HMF conversion was 93.7% with a HMFCA yield of 79.1% after 12 h.

Oxidation of HMF into HMFCA using various oxidants

In order to explore the scope of the catalytic system for the oxidation of HMF, the oxidation of HMF was carried out using various oxidants. As shown in Table 4, the oxidant species showed a remarkable effect both on HMF conversion and HMFCA yield. When *t*-BuOOH was used as the oxidant, the HMF conversion reached 100% (Table 4, entry 1). However, no furan compound such as HMFCA, DFF, and FDCA were detected by HPLC (Table 4, entry 1). Based on the above data, we can conclude that the furan ring of HMF would be destroyed during the oxidation process by the strong oxidant *t*-BuOOH. In contrast to *t*-BuOOH, the oxidation reaction occurred with difficulty using H_2O_2 as the oxidant (Table 4, entry 2). Molecular oxygen was found to be the best oxidant in the aerobic oxidation of HMF into HMFCA. A high HMFCA yield of 86.9% and HMF conversion of 100% were obtained after 3 h with the flushing of oxygen at a rate of 20 mL min^{-1} (Table 4, entry 3). These good results encouraged us to carry out the oxidation of HMF using an oxygen balloon instead of with the flushing of oxygen, and the K-10 clay-Mo catalyst also showed high catalytic activities (Table 4, entries 4 & 5). It only required 4 h to obtain a high HMFCA yield of 86.1% and HMF conversion of 100% (Table 4, entry 5). The oxidation reaction was further conducted in an air atmosphere, and it still showed excellent results (Table 4, entries 6 & 7). However, a long reaction time of 8 h was required to obtain a HMF conversion of 100% and HMFCA yield of 83.6% (Table 4, entry 7), which is due to the low concentration of molecular oxygen in the solution. The oxidation reaction in the air makes the developed method much more convenient and economical.

Time course of the aerobic oxidation of HMF into DFF

In order to obtain deeper insights into the catalytic aerobic oxidation of HMF into HMFCA over K-10 clay-Mo, the content of HMF and the oxidation products at different reaction time points were recorded. The main product of the aerobic oxidation of HMF was HMFCA, and DFF was detected as the only oxidation product during the aerobic oxidation of HMF into HMFCA over K-10 clay-Mo. As shown in Fig. 6, the content of HMF decreased gradually during the reaction process, and the content of the main oxidation product HMFCA increased gradually with the increase of the reaction time. HMF was completely converted after 3 h, and the highest HMFCA yield of 86.9% was obtained. In addition, the yield of the byproduct

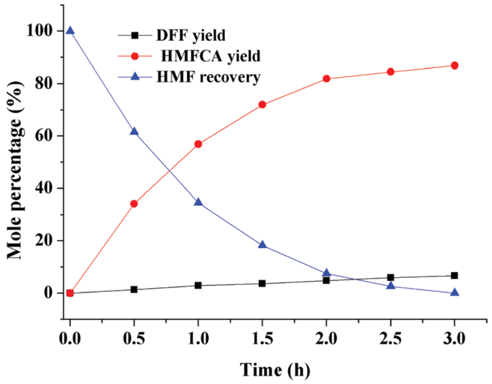

Fig. 6 Time course of HMF recovery and product distribution during the process of the aerobic oxidation of HMF. Reaction conditions: HMF (70 mg) and K-10 clay-Mo (150 mg) were added to toluene (7 mL), and the reaction was carried out at 110 °C for 3 h with the flushing of dioxygen at a speed of 20 mL min^{-1}.

DFF also increased gradually during the reaction course, but the increase rate was slow. The DFF yield only reached 6.7% after 3 h. The results indicated that the oxidation of aldehyde into acid is much easier than the oxidation of hydroxyl into aldehyde when the aerobic oxidation of HMF was catalyzed by K-10 clay-Mo. Thus, a high HMFCA yield and selectivity were obtained in our reaction system. In addition, after 3 h, a HMFCA yield of 86.9%, DFF yield of 6.7%, and FDCA yield of 1.8% (data not given) were obtained. The total of the determined furan compounds reached up to 95.4%, which was close to the HMF conversion. The results indicated that the furan ring was not destroyed when O_2 was compared with *t*-BuOOH as the oxidant as discussed above.

Catalyst recycling experiments and product identification

The reusability of a heterogeneous catalyst is one of the most important benefits and makes it useful for commercial applications. The recovery and reusability of the K-10 clay-Mo catalyst was studied, and the aerobic oxidation of HMF was used as a model reaction. At the end of the reaction, the catalyst was separated by simple filtration. Then it was washed with ethanol and dried in vacuum at 100 °C over night. The reused catalyst was used for the second cycle under the same reaction conditions. These processes were repeated for five times to test the stability of the catalyst. As shown in Fig. 7, the yield of HMFCA remained almost stable for cycle during the recycling experiments (86.9% in first cycle *versus* 83.9% in sixth cycle). These results indicated that the K-10 clay-Mo catalyst was stable during the reaction without the leaching of Mo into the reaction system. The resulting catalyst could be reused without any significant loss of catalytic activity.

In order to further verify the stability of the K-10 clay-Mo catalyst during the reaction process, the leaching experiment was also carried out. As shown in Fig. 8, the aerobic oxidation of HMF was firstly carried out at 110 °C for 1 h in toluene with the oxygen flow rate at 20 mL min^{-1}, then the catalyst was filtered off. The reaction solution in the absence of the catalyst was subjected to stirring at 110 °C for another 2 h under otherwise the same conditions. As shown in Fig. 7, the HMFCA yield was maintained at a stable level of 57.2% from 1 h to 3 h. These results also indicated that there was no leaching of Mo during the reaction, which once again indicated that the catalyst was stable during the reaction process. Our results were consistent with the results reported by Farias *et al.*, in which they used the same catalyst for the epoxidation of vegetable oils using *t*-BuOOH as the oxidant in toluene.[27] The results indicated that $MoO_2(acac)_2$ chemically bonded with the K-10 clay support. In addition, the reaction solution was also analyzed by ICP-AES, and there was no Mo detected in the reaction solution.

Developing a facile and economical method to obtain purified product is also a very crucial goal in terms of green chemistry. When the reaction mixture in toluene was cooled to room temperature, HMFCA was precipitated out from the solvent in the form of needle-like crystals with a yellow color.

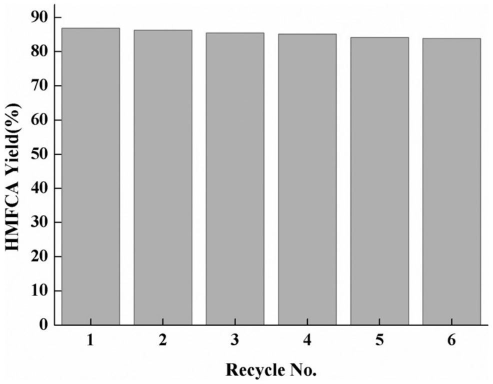

Fig. 7 The recycling experiments of the K-10 clay-Mo catalyst on the aerobic oxidation of HMF into HMFCA. Reaction conditions: HMF (70 mg) and K-10 clay-Mo (150 mg) were added into toluene (7 mL), and the reaction was carried out at 110 °C for 3 h with the flushing of dioxygen at a rate of 20 mL min^{-1}.

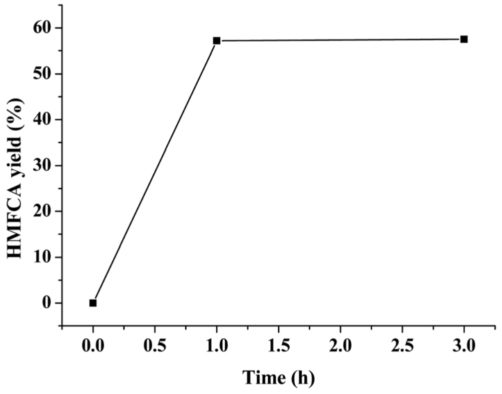

Fig. 8 The results of the leaching experiment for the aerobic oxidation of HMF into HMFCA catalyzed by K-10 clay-Mo by hot filtration after 1 h. Reaction conditions: HMF (70 mg) and K-10 clay-Mo (150 mg) were added to toluene (7 mL), and the reaction was carried out at 110 °C for 3 h with the flushing of dioxygen at a speed of 20 mL min^{-1}.

However, limited HMFCA and by-product DFF remained in the solvent. The toluene solvent could be readily purified by evaporation under reduced pressure due to the large boiling points between toluene and the furan compounds. Thus, the solvent can be reused. The precipitated HMFCA was then easily purified by washing several times with ethyl acetate. The resulting HMFCA was characterized by ^{1}H NMR and ^{13}C NMR. The NMR data were recorded as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.1 (s, 1H, –COOH), 7.23–7.22 (d, 1H, J = 4.0 Hz, furan ring), 6.59–6.58 (d, 1H, J = 4.0 Hz, furan ring), 4.65 (s, 2H, –O–CH_2-furan ring), 1.60 (s, 1H, –OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.5, 157.2, 152.8, 121.8, 111.8, 64.6.

Conclusion

In this study, a molybdenum(VI) complex was successfully immobilized on K-10 clay by the cation exchange method. The heterogeneous K-10 clay-Mo catalyst showed high catalyst activity and selectivity in the oxidation of HMF into HMFCA with molecular oxygen. Under optimal conditions, a HMF conversion of 100% and HMFCA yield of 86.9% were obtained after 3 h with the flushing of oxygen at 110 °C. The activity of the K-10 clay-Mo catalyst is robust, as the oxidation reaction could occur smoothly in air. More importantly, the catalyst was stable during the reaction, and could be reused several times without loss of its activity. These methods represent an interesting and highly atom-efficient alternative for the oxidation of aldehyde groups into carboxylic groups, as oxygen is cheap, readily available, and an oxidant that produces water as the only by-product.

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