

The mixture of samples was analyzed by high-performance chromatography with UV detection (278 nm) and a 996 photodiode array detector. The 996 photodiode array detector characterized the product distribution of HFM, HMFCa, FFCA, DFF and other byproducts from the oxidative cleavage of furan ring of HMF. In addition, UV absorption of HFM and HMFCa was almost at the same wave length (deviation or error < 2%). The selectivity of HMFCa and FFCA was calculated based on the carbon balance.

$$m_1 = \frac{W}{\frac{A'}{A} - 1}$$

m_1 : mass of HMF after reaction

A' : HPLC areas of HMF when 0.03g HMF added;

A : HPLC areas of HMF after reaction;

W : The mass of HMF added, 0.03g.

$$\text{HMF conversion (mas\%)} = \left(1 - \frac{m_1}{m_2}\right) \times 100\%$$

M_2 : mass of HMF before reaction

$$\text{Selectivity of FDCA} = \frac{S_1}{S_1 + S_2 + \dots}$$

S : HPLC areas of reaction products

After reaction mixture was diluted with alcohol (10 mL), the catalyst precipitated from solution, and it was obtained by filtration. The recycled experiments were conducted, and reaction results were shown in supported Table 1. The selectivity of FDCA was 99.3%, and the conversion of HMF is 100%. After the fourth recycling,

the selectivity of FDCA was about 97.6% and the conversion of HMF was 97.7%. The results indicate that the $[\text{EMIM}]_4\text{Mo}_8\text{O}_{26}$ was stable during the reaction process without the loss of its catalytic activity.

Support table 1. Performance of $[\text{EMIM}]_4\text{Mo}_8\text{O}_{26}$

Entry	Recycle number of $[\text{EMIM}]_4\text{Mo}_8\text{O}_{26}$	Product Selectivity (mol%)			Conversion (HMF %)
		FDCA	HMFC	Cleavage	
1	1	99.5	0.5	-	100
2	2	99.3	0.7	-	100
3	3	99.0	1	-	99.5
4	4	97.6	1.60	0.8	97.7

Conditions: 9 mmol HMF, 18 mmol NaOH, the mass ratio of HMF to $[\text{EMIM}]_4\text{Mo}_8\text{O}_{26}$ is 1/10, 20 ml deionized water as reaction solvent, 25 ml 6% H_2O_2 as oxidant and reaction temperature 100 °C.