Metal organic frameworks supported of ceramic foams for cyclohexene and benzyl alcohol oxidation

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INTRODUTION

Metal Organic Frameworks is a new family of microporous materials distinguished by a large specific surface and versatile use in many areas. Their structure consists of metal clusters and organic ligands. As a result of the exchange of ligands and linkers, it is possible to obtain unique properties [1].

HKUST-1 (Hong Kong University of Science and Technology) is used as a heterogeneous catalyst in many chemical reactions. There are many studies on the modification of the catalyst structure in order to obtain the best possible catalytic, chemical and mechanical properties. The next step is to obtain structured catalysts [2].

MATERIALS AND METHODS

The catalyst preparation process consisted of 3 stages. The prepared ZrO_2 foams were cleaned by sonication in acetone to remove air and impurities. In the next stage, M (M = Cu; CuCo; CuPd)-HKUST-1 was deposited in situ using the solvothermic method [3]. 2 mmol of trimesic acid was dissolved in 12 ml of ethanol. Accordingly, 3.6 mmol $Cu(NO_3)_2$ * $3H_2O$ (Cu-HKUST-1); 2.9 mmol $Cu(NO_3)_2$ ·$3H_2O$ and 0.72 mmol (CuCo-HKUST-1); 3.4 mmol $Cu(NO_3)_2$ · $3H_2O$ and 0.22 mmol $Pd(NO_3)_2$ · $2H_2O$ (CuPd-HKUST-1) was dissolved in 12 ml of deionized water . Finally, the obtained solution was mixed and heated at 110 °C for 18h. In the activation step, the catalyst was washed with ethyl alcohol and water, dried and heated at 110 °C under vacuum.

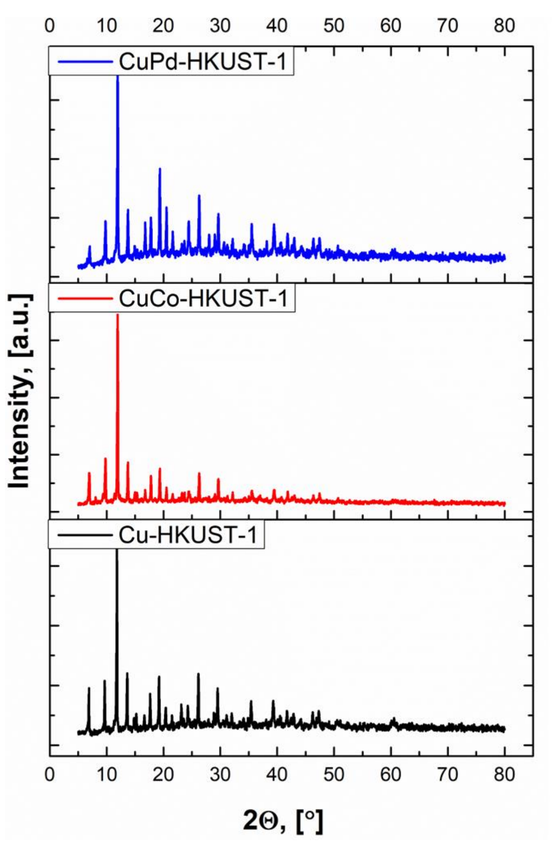


Figure 1 XRD analysis of prepared materials.

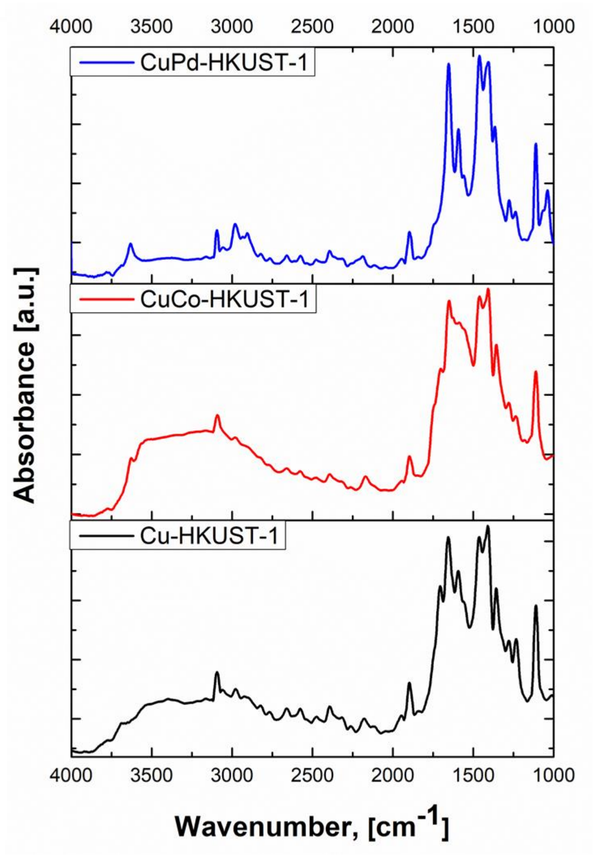
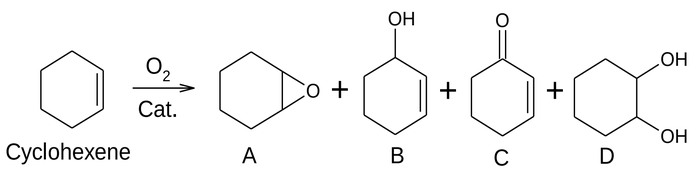
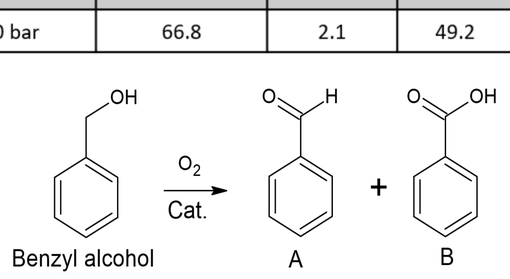


Figure 2 DRIFT spectra of activated samples (wafers).

Table 1 Results of catalytic activity of prepared samples in aerobic oxidation of cyclohexene and benzyl alcohol.



MOF sample		Pressure	Conversion [%]	Selectivity [%]				
				A	B	C	D	other
blank		10 bar	10.0	6.3	64.0	16.1	4.5	9.1
Cu-HKUST-1	powder	10 bar	75.7	0.5	43.3	49.6	5.3	1.2
	ZrO_2 foam	10 bar	64.9	6.1	51.3	38.3	1.7	2.6
CuCo-HKUST-1	powder	10 bar	33.4	1.7	35.3	57.0	3.5	2.4
	ZrO_2 foam	10 bar	64.5	4.6	46.4	44.8	1.9	2.2
CuPd-HKUST-1	powder	10 bar	61.8	0.9	41.8	49.3	5.6	2.3
	ZrO_2 foam	10 bar	66.8	2.1	49.2	43.0	4.5	1.2



MOF sample		Pressure	Conversion [%]	Selectivity [%]		
				A	B	other
blank		10 bar	5.3	89.5	10.5	0.0
Cu-HKUST-1	powder	10 bar	12.5	100.0	0.0	0.0
	ZrO_2 foam	10 bar	10.7	98.8	0.0	1.2
CuCo-HKUST-1	powder	10 bar	19.5	100.0	0.0	0.0
	ZrO_2 foam	10 bar	14.1	98.9	0.0	1.1
CuPd-HKUST-1	powder	10 bar	62.5	96.6	3.4	0.0
	ZrO_2 foam	10 bar	26.9	99.2	0.0	0.8

Table 2 Results of the nitrogen adsorption for prepared samples; A) N_2 adsorption measurements for powder M(M=Cu; CuCo; CuPd)-HKUST-1 samples, B) N_2 adsorption measurements for deposited M(M=Cu; CuCo; CuPd)-HKUST-1/ZrO_2 foam referred to deposited MOF mass.

A) Powder samples M(M=Cu; CuCo; CuPd)-HKUST-1 powders		B) M(M=Cu; CuCo; CuPd)-HKUS-1/ZrO_2 foam referred to deposited MOF mass	
N_2 adsorption measurement	S_{BET}, [m^2/g]	N_2 adsorption measurement	S_{BET}, [m^2/g]
Cu-HKUST-1	1270.0	Cu-HKUST-1	448.0
CuCo-HKUST-1	1254.3	CuCo-HKUST-1	639.9
CuPd-HKUST-1	1326.0	CuPd-HKUST-1	654.5

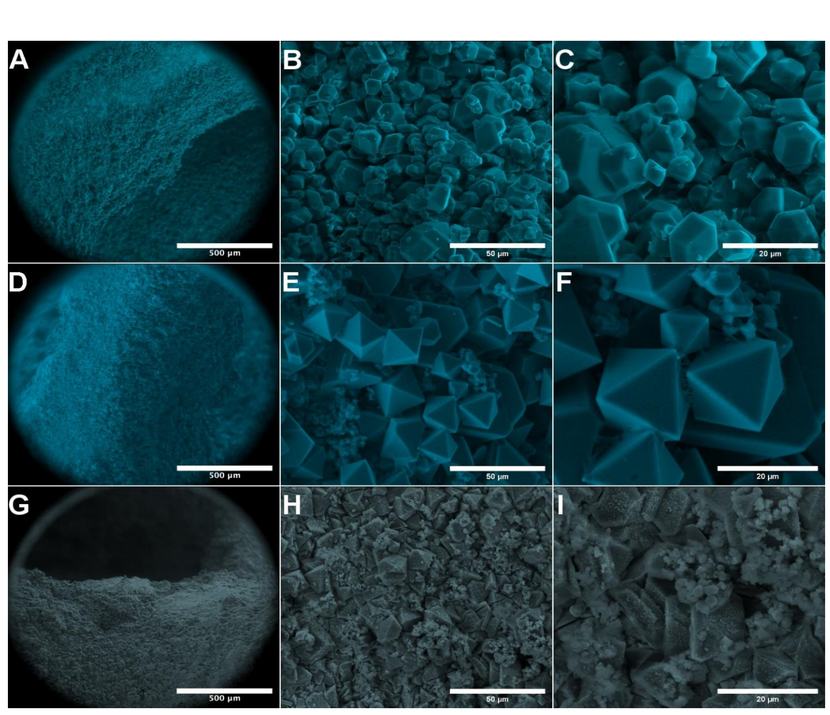


Figure 3 SEM images of M(M=Cu; CuCo; CuPd)-HKUST-1 deposited on ZrO2 foam; A-C) Cu-HKUST-1, D-F) CuCo-HKUST-1, G-I) CuPd-HKUST-1.

CONCLUSIONS

The aim of the work was to develop and characterize structured HKUST-1 catalysts using spectroscopic and microscopic methods and to determine their catalytic abilities in the processes of catalytic oxidation of cyclohexene and benzyl alcohol. The MOF layer deposited on ceramic foams was characterized and its molecular structure and surface morphology determined. The tested catalysts in the form of powders and structured MOFs on foams showed catalytic activity in the proposed reactions with a conversion above 60% for the cyclohexane oxidation reaction except for CuCo-HKUST-1 powder and a conversion ranging from 10.7% - 62.5% for the benzyl alcohol oxidation reaction. There is an increase in the conversion of the cyclohexene oxidation reaction for CuCo-HKUST-1 and CuPd-HKUST-1 materials using a structured catalyst instead of a powder. The advantage of using HKUSTs mounted on foams is that the problem of removing and filtering the catalyst from the post-reaction mixture is avoided.

REFERENCES

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