Hydrogenolysis of 5-HMF into DMF via non-Noble bimetallic Cu-Fe catalyst

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Abstract: Hydrogenolysis of 5-HMF was performed over non-Noble bimetallic Cu-Fe catalyst which was synthesized by simple co-precipitation method. Catalyst was extensively characterized by XRD, XPS, TEM, SEM and NH_3-TPD to establish structure-activity correlation. Catalysts with different metallic ratios were screened, out of which Cu-Fe (1:2) was found most efficient with 93% conversion and 91% selective to DMF. Reaction was studied extensively and all the reaction parameters were optimized.

Keywords: DMF, Fuel additive, Hydrogenolysis.

1. Introduction

Continuous depletion of fossil fuel resources and rapidly increasing fuel demand is a great challenge for current scientific community to find out the alternatives of currently available non-renewable energy sources (1-2). Biomass derived C5 platform molecule 5- HMF is considered as one of the alternative for the sustainable future. 5-HMF can be converted into a variety of fine chemicals like FDCA, BHMF, GVL, DFF, and DMTHF which are useful in polymer industry, pharmaceuticals and petrochemicals (3). Hydrogenolysis of 5-HMF produces 2, 5-dimethyl furan (DMF) which is a promising fuel additive because of its attractive property like high energy density, ideal boiling point and high research octane number (4). Its immiscibility with water led to its economic processing in refinery which makes it prominent competitor of bioethanol.

2. Experimental

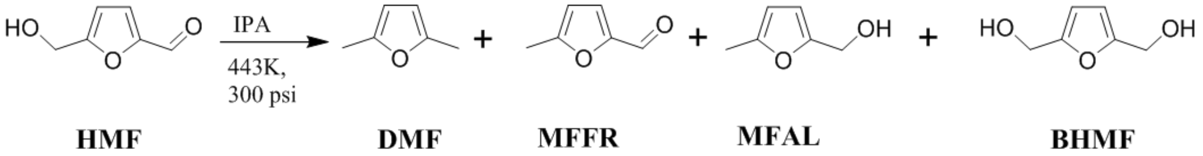
All the catalysts were prepared by co-precipitation method. Calculated amount of nitrate precursors were dissolved in DI H_2O. 2M solution of the precipitating agent (NaOH) was added in the aqueous solution of metal precursors. The pH of the solution was maintained at 10. After complete addition of precipitating agent the solution was stirred for overnight. The as obtained slurry was filtered, washed and dried at 373K for 16h and further calcined at 723K with the rate of 5°C/min for 5h. Before use, this calcined catalyst was further activated by H_2 flow of 2 ml/min at 523K with the heating rate of 2°C/min.

All the catalytic reactions were carried out in 45mL stainless steel Parr autoclave. 100mg HMF was dissolved in 20mL of 2-Propanol along with 50mg of catalyst. The reactor was purged for 2 times with N_2 gas before pressurizing with external Hydrogen. The reaction was conducted at 443K temperature, 300 psi external H_2 pressure for 4h. Reaction aliquots were taken at regular interval of 1h and analyzed over GC-FID equipped with HP-5 capillary column.

3. Results and discussion

Hydrogenolysis of 5-HMF was conducted with the aim to achieve high efficiency for the Cu-Fe bimetallic catalyst. The major objective of this work was to bring down the harsh conditions usually practiced in the non-noble metal hydrogenolysis of 5-HMF and proposing a non-precious efficient catalyst. Various metal ratios were screened for the Cu-Fe. The detailed results are shown in Table1. The conversion and selectivity were tuned with different metal loading of Cu and Fe. When Cu used in excess amount [Cu-Fe (2:1)] the conversion was increased to 95% form 91% but selectivity was somewhat less than that shown by Cu-Fe (1:2). The selectivity for Cu-Fe (2:1) was 89% whereas; it was 93% for Cu-Fe (1:2). Catalytic synergism between Cu and Fe was responsible for the increased conversion. Plausible reaction pathway was proposed after performing several controlled experiment as shown in Scheme 1.

Reaction Scheme:



Scheme 1: Hydrogenolysis of 5-HMF (**Reaction Conditions**: 5-HMF =100mg, catalyst=50mg, IPA=20ml, T=443K, P=300 psi, t=4h).

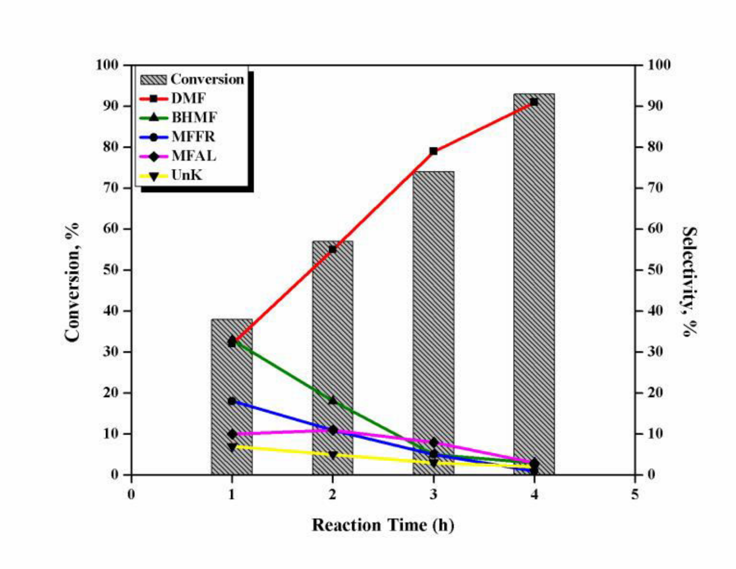


Figure 1. Conversion-time profile for the hydrogenolysis of 5-HMF (**Reaction Conditions**: 5-HMF =100mg, catalyst=50mg, IPA=20ml, T=443K, P=300 psi, t=4h).

Sr.No.	Catalysts	Conversion (%)	Selectivity (%)				
			DMF	BHMF	MFFR	MFAL	UnK
1	CoOx-NP	47	10	8	11	9	62
2	CuOx-NP	82	59	8	19	10	4
3	FeOx-NP	39	12	25	28	17	18
4	Cu:Fe(1:1)	85	72	10	3	9	6
5	Cu:Fe(2:1)	95	89	2	1	5	3
6	Cu:Fe(1:2)	93	91	3	1	3	2

Table 1. Catalyst's screening for the hydrogenolysis of 5-HMF. (**Reaction Conditions**: 5-HMF =100mg, catalyst=50mg, IPA=20ml, T=443K, P=300 psi, t=4h).

4. Conclusions

Cu-Fe (1:2) proved highly efficient and economic bimetallic catalyst for the hydrogenolysis of 5-HMF. Selectivity tuning was done by using different metal ratios. Catalyst was characterized to establish structure-activity correlation. It was observed that synergism in metallic phase of Cu and Fe played a significant role in high efficiency of catalyst. Further work on detail of structural characterization of catalyst and process parameters optimization is in progress.

References

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