

Single Pot Transformation of Furfural to 2-Methyltetrahydrofuran Over Pd Supported Hydrotalcite Catalysts

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Abstract: Co-Al hydrotalcite was prepared by a co-precipitation method. As prepared hydrotalcite used as for support on which Pd was loaded by wet impregnation method with their chloride precursor. The prepared catalyst was characterized by XRD, XPS, TEM and NH₃-TPD. Among various Pd loadings and Co-Al ratios of HT's, 2 % Pd/ Co-Al₁₂ catalyst exhibited excellent performance giving complete conversion of FFR and the highest selectivity of 73% to 2-MeTHF. Based on structure characterization and several controlled experiments carried out, a plausible reaction pathway for the formation of 2-MeTHF. Successful recycling of the catalyst was also established.

Keywords: Furfural, 2-methyl tetrahydrofuran, Pd/Co-Al.

1. Introduction

Furfural is one of the most important platform molecule derived from biomass via acid catalysed dehydration of arabinose and xylose which has great potential to get transformed to various useful chemicals and fuel compounds. There have wide applications in production of natural and synthetic resins, intermediates in pharmaceutical industries and food industries etc¹⁻³. Out of there, 2-MeTHF is such a value added product having water miscibility and viscosity; it is widely used in chemical industries replacing THF. According to new DOE report, it is identified as a second generation P-series fuels compared to traditional use of gasoline because of its lower heating value and high energy density⁴⁻⁶.

2. Experimental

All the mixed metal HT materials were prepared by co-precipitation method using appropriate amounts of respective metal precursors and NaOH with K₂CO₃ as a precipitating agent. The pH of solution was maintained in between the range of 9-10. The cake thus obtained was filtered, washed and calcined then used as a support for next step catalyst preparation, Pd/HT catalysts were prepared by wet impregnation method using acidic (HCl) solution of PdCl₂. The catalytic reactions were performed in a 300 mL stainless steel autoclave equipped with overhead stirrer, a pressure gauge and automatic temperature control facility. 2.5 g furfural, 90 mL (IPA) solvent and 0.25 g were charge to the reactor, pressurised with H₂ after attaining the desired temperature. Liquid samples were analysed using GC equipped with HP-5 capillary column. Performance of all catalysts was evaluated in terms of (%) conversion of FFR and (%) product selectivity w.r.t. moles.

3. Results and discussion

In the present work, hydrotalcite supported palladium catalysts were studied for hydrogenation of furfural to yield the maximum conversion and highest selectivity towards ring hydrogenation product i.e 2-MeTHF. Later, maximum selectivity could be tailored by integrating catalyst design with the optimization of reaction conditions. Among various Pd loadings on HTs, 2 % Pd/ Co-Al (12) catalyst showed excellent performance in terms of FFR conversion and gives the highest selectivity to 73% to 2-MeTHF (Table 1). Appropriate metal loading, different phases of palladium species attributed to absorb furfural molecules on surface through C=C bond and C=O bonds which is responsible for highest selectivity of 2-MeTHF (Figure 1)^{7,8}. Formation of both FAL & 2-MF was observed at initial stage which leads to the formation of 2-

MeTHF (Figure 2). Several controlled experiments were also performed, the results of which combined with the characterization data allowed to propose a plausible reaction pathway for the formation of 2-MeTHF.

Table 1. Effect of metal loading on conversion and selectivity.

Sr. No.	Catalyst	Conv., %	Selectivity, %					
			FAL	THF	THFAL	2-MF	2-MeTHF	Others
1	1% Pd/CoAl-12	>99	-	1	19	15	43	22
2	2% Pd/CoAl-12	>99	-	3	18	0	73	6
3	4% Pd/CoAl-12	>99	-	3	13	5	68	10

Reaction conditions: Furfural, 2.5g; Solvent (IPA), 95ml; loading, 0.25g; Temp., 220 °C; pressure, 500 psig, reaction time, 5h.

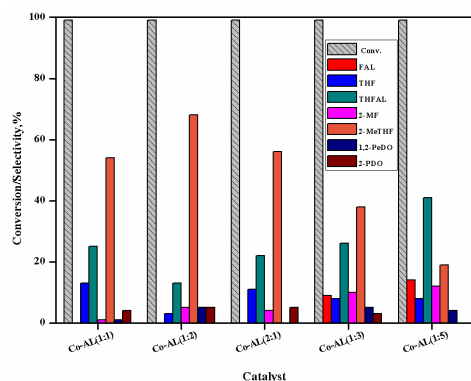


Figure 1. Effect of Co-Al ratio

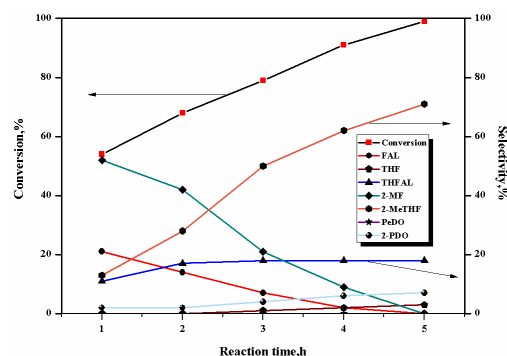


Figure 2. Conv. Vs time profile

4. Conclusions

Various Pd supported Co-Al based hydrotalcites were prepared by varying Co and Al composition and were eventually made possible for achieving the product selectivity tuning in the single step hydrogenation of FFR to 2-MeTHF. Amongst them, 2PdCoAl12 showed excellent results giving 73% selectivity for 2-MeTHF and rest of THFAL (18%) with least amount of other byproduct. Systematic study of different phases of Co-Al was done by XRD and XPS analysis which drastically enhances the selectivity of 2-MeTHF. The ring hydrogenation reaction could also be controlled by manipulating the reaction parameters such as temperature and H₂ pressure. The efforts to enhance the selectivity to 2-MeTHF through catalyst modification is being continued.

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