Kinetics Study of the Hydrogenation/Deoxygenation of Furfural and Methyl Furfural over Supported Metal Catalysts

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Introduction

Pyrolysis oils (or bio-oils) contain a wide variety of oxygenated compounds such as sugars, furfurals, carboxylic acids, aldehydes, carbohydrate derivatives, phenols, etc.,[1]. In order to make bio-oil more fungible with standard gasoline and diesel, deoxygenation of these oxygenated compounds is needed [2]. We have started a systematic study of deoxygenation kinetics of a series of oxygenated compounds, representative of bio-oil constituents, on different metal catalysts (Pt, Pd, Cu). The present contribution compares the kinetics of furfural and methyl furfural deoxygenation on Cu catalysts, with and without addition of other typical constituents (e.g. water, acetic acid, etc.).

Materials and Methods

A 5 wt % Cu/SiO_2 (HiSil210) catalyst was prepared by incipient wetness impregnation. The rates of furfural and 5-methyl furfural hydrogenation and deoxygenation were measured at atmospheric pressure in a flow reactor in excess hydrogen (liquid feed rate=0.5 ml/h, H_2 feed rate=60 ml/min) with on-line gas chromatographic analysis. The temperature range investigated was 230°C-290°C; the space time (W/F) ranged from 8 to 50 g.cat h/mol.

Rate data for all the reactions in the temperature range investigated were found to be very well represented by single-site Langmuir-Hinshelwood kinetics, with kinetic (e.g. activation energies) and adsorption parameter (e.g. heat of adsorption) values that are in good agreement with literature data.

Results and Discussion

Table 1 summarizes the results of the fitting resulting from combining all the experimental runs at varying temperatures, W/F, and initial compositions. To test the validity of the model, several mixtures of products and reactants were fed to the reactor and the evolution of their concentration as a function of W/F compared with the values predicted by the model. Perfect agreement was found each time.

The inhibiting effect of the presence of water on furfural conversion was quantified. Interestingly, since the heat of adsorption of water is high, but the entropic pre-exponential factor is rather low, the competing effect of water on hydrogenation/deoxygenation rate is high at lower temperatures (230°C), but it is practically negligible at higher temperatures (290°C).

Similar kinetics studies were conducted with methyl furfural. As opposed to the case of furfural, for which it is possible to find conditions that lead to high selectivity to the intermediate furfuryl alcohol, with methyl furfural as a feed, no alcohol was observed under any of the conditions investigated, but only the final product dimethyl furan. The kinetic analysis indicates that the rate of conversion of the methyl furfuryl alcohol is much faster than the furfuryl alcohol.

From the point of view of fuel upgrading it is important to determine what is the most desirable extent of conversion based on the fuel properties. That is, the octane number of the furfuryl alcohol is slightly higher and vapor pressure much lower than that of the methyl furan; therefore, one may want to maximize the intermediate product. However, the solubility in water is another important fuel property that determines the fungibility of fuel components. In this sense, the methyl furan would be a more attractive product.

Table 1. Kinetic and Adsorption Parameters Obtained by Fitting Furfural and 5-Methyl Furfural Rates of Conversion with a Single-Site Langmuir-Hinshelwood Model.

Temp. (°C)	Equilibrium constant K_{eq}	Kinetic constant k_1	k_2	k_{-1}
230	5.570	0.981	0.041	0.176
270	3.654	2.335	0.103	0.639
290	2.470	3.441	0.156	1.393

Heat of Adsorption	kcal/mol
Furfural	12.332
Furfuryl alcohol	6.922
2-Methyl-furan	3.654
Water	12.365

Activation Energy (cal/mol)	
E_1	11768.15
E_2	12436.00

Temperature (°C)	k
230	0.11
250	0.25
270	0.52
290	1.24

E_a = 22.8 kcal/mol

References

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