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Catalytic hydrodeoxygenation of anisole: an insight into the role of metals on transalkylation reactions in bio-oil upgrading

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1. Materials

All chemicals used, including anisole, phenol, toluene, benzene, were bought from Fisher Scientific. Commercial benchmark catalysts $NiMo/Al_2O_3$ was purchased from Alfa Aesar. The Ni and Mo loadings on $NiMo/Al_2O_3$ are 4.2 wt.% and 11.4 wt.%, respectively. The catalyst was activated by flowing dimethyl disulfide in toluene (3%) with hydrogen to the reactor for 3 hours. MoP/Al_2O_3 [1] and Ru/Al_2O_3 [2] were synthesized in the lab using the literature methods. Ru loadings on Ru/Al_2O_3 is 6 wt%. MoP catalyst was prepared by incipient wetness impregnation of Al_2O_3 support using equimolar Mo and P solutions formed from ammonium paramolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, and ammonium phosphate, $(NH_4)_2HPO_4$. Quantity was adjusted to obtain loading of Mo of 13 wt % (1.04 mmol/g). The impregnated support was calcined in air at 500°C for 6 h. The resulting solids was activated by hydrogen in the reactor before use.

2. Catalytic experiments

The catalytic experiments were carried out by using a 1/2-inch O.D., 24-inch long, 316L stainless tubular reactor at about 20 psig hydrogen pressure. In each run, the catalyst sample (10 g, 20 mesh) was packed in the reactor between two layers of quartz wool. The reactor was stationed in a temperature-programmed furnace. A 3/8-inch O.D., 16-inch long, tubular stainless-steel reactor was used as a preheater which was equipped with a temperature controller. At the beginning of the experiment, the temperature of the reactor was increased at 20◦C/min and held at the desired value for 0.5 h in flowing N_2 (100 mL/min) before reaction. When the temperature stabilized, 10 wt.% anisole or

phenol in toluene was fed by a high-pressure Eldex pump at a desired liquid flow rate and vaporized before entering the reactor. Gas flow was adjusted by a Rotameter. All pipelines were insulated to avoid condensation of either reactants or products.

3. Analysis and calculation methods

The effluent was trapped in a container placed in an ice-water bath, and analyzed by GC-FID and GC–MS (Shimadzu QP2010s) with the same polyethylene glycol column (50mx200μmx40μm). The GC and GC-MS analytical conditions are as follows: inlet: 225°C, Split Mode 200:1, 1 □L (neat) injection; oven: 50°C-5min, 15°C/min, 250°C. Phenol and hexamethylbenzene were used as external standards for phenolic products and alkybenzenes products, respectively. The conversion of reactants and the distribution of products were calculated based on the following methods.

$$Coversion\ = \frac{R0 - R1}{R0} \times 100\%$$

R0=Reactant initially added, R1=Reactant remaindered

$$Distribution\ X = \frac{Yieldx}{Total\ product\ yield} \times 100\%$$

Yield x=4×10^{-8}A-0.3502 (X contain phenolic hydroxyl group, A=GC area, phenol was used as standard)

Yield x=1×10^{-8}A+0.0004 (X does not contain phenol hydroxyl group, A=GC area, Hexamethylbenzene was used as standard)

4. External standard curves

4.1. Quantitative Analysis of phenol by GC

Table S1. GC Analysis of Different Standard Concentrations of Phenol

Area Counts	Phenol wt%
0	0
54033117.5	1.802
136836605	4.826
229002567.5	8.807
503932756.5	20.186

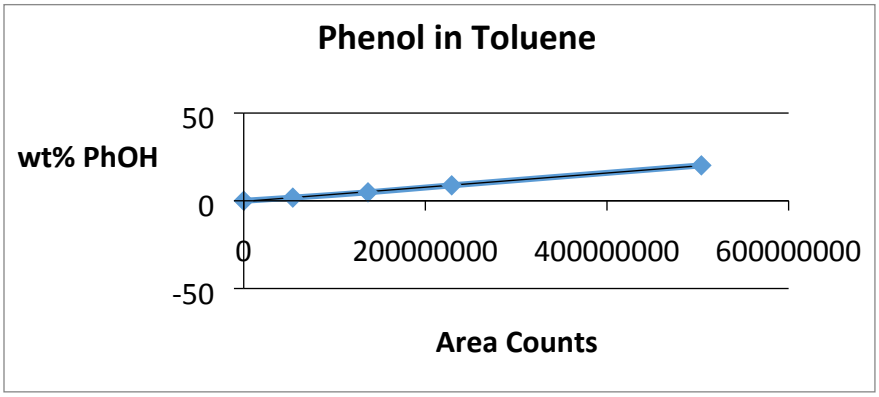

Figure s1. External standard curve of phenol

4.2. Quantitative Analysis of Hexamethylbenzene by GC

Tables 2. GC Analysis of Different Standard Concentrations of Hexamethylbenzene

Area Counts	Hexamethylbenzene wt%
0	0
7657945	0.09
15330304	0.19
21640603	0.28
45345956	0.56
75730480	1.12

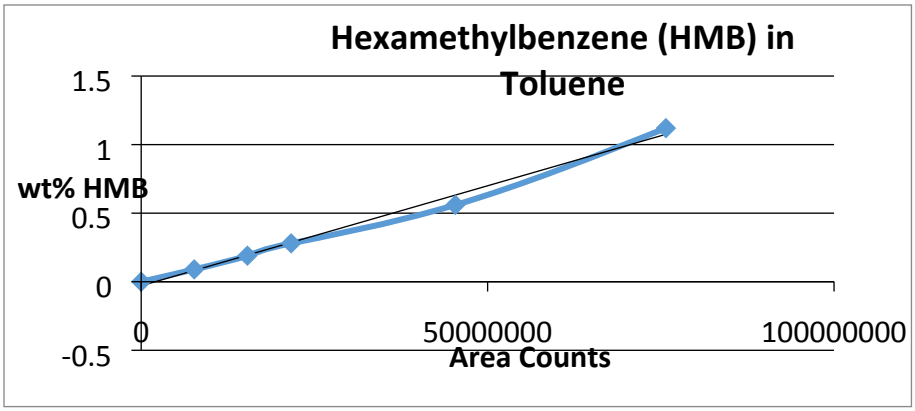

Figure s2. External standard curve of hexamethylbenzene

References

(1) S. T. Oyama, P. Clark, V. L. S. Teixeira da Silva, E. J. Lede, and F. G. Requejo, XAFS Characterization of Highly Active Alumina-Supported Molybdenum Phosphide Catalysts (MoP/Al_2O_3) for Hydrotreating, *J. Phys. Chem*. B 2001, **105**, 4961-4966.

(2) Vanina A. Mazzieri, Pablo C. L'Argentiere, Fernando Coloma-Pascual, and Nora S. Fıgoli, Effect of Chlorine on the Properties of Ru/Al_2O_3, *Ind. Eng. Chem. Res.* 2003, **42**, 2269-2272.