

Hydrodeoxygenation of 4-Methylphenol over Mo Catalysts

Victoria M. L. Whiffen and Kevin J. Smith*

Department of Chemical and Biological Engineering, University of British Columbia
2360 East Mall, Vancouver, British Columbia V6T 1Z3 (Canada)
vwhiffen@chml.ubc.ca and *kjs@interchange.ubc.ca

Introduction

Bio-oils derived from the pyrolysis of bio-mass contain high amounts of oxygen (>10 wt.%) that contribute to the low heating value, high viscosity, and instability of these oils [1]. Removal of the oxygen by hydrodeoxygenation (HDO) of bio-oils has been mostly reported over Co/Ni promoted MoS₂ catalysts [2]. Furimsky et al. investigated the HDO of substituted phenols using oxidic and sulfided CoMo/Al₂O₃. Overall, the conversion over the two catalysts was similar [3]. Matsuda et al. have shown that bulk MoO₃ with a surface area of 5 m²/g can be transformed into a microporous MoO_x catalyst with an increased surface area of 180 m²/g after reduction in H₂ at 623 K [4]. Bunch and Ozkan concluded that reduced MoO_x catalysts carry out the same hydrogenolysis function as sulfided catalysts for the HDO of benzofuran [2]. The objective of this study is to further examine the effect of the oxidation state and ligand of Mo catalysts on the HDO of 4-methylphenol.

Materials and Methods

Reactions were carried out in a 300 mL stirred-batch reactor at 598–648 K and 4.14–4.83 MPa H₂. 4-Methylphenol (4MP) was used as a model reactant at 2.96 wt% in 100 mL decalin. The reactant solution was slurried in the reactor with 11,000 ppm Mo catalyst. MoS₂, MoO₂, and MoO₃ (Sigma Aldrich) were tested without pretreatment. The catalysts were characterized by means of XRD, TPR, and BET analysis. Reaction products were identified and quantified via GC/MS analysis. The experimental data were used to examine the reaction pathway and kinetics of the reaction.

Results and Discussion

Toluene was the main reaction product over MoO₂, MoS₂, and MoO₃ catalysts. Hydrogenation products methylcyclohexane, 1-methylcyclohexene, and 4-methylcyclohexene were also produced. Small amounts of isomerization products, such as ethylenecyclopentane, ethylcyclopentane, 1,3-dimethylcyclopentane, and 4,4-dimethylcyclopentene were detected. Table 1 displays the selectivity of the quantified products from the HDO reaction at 598 K and 4.14 MPa. The product distribution for the HDO of 4MP over MoO₃ was found to be a strong function of temperature. As the temperature increased the degree of hydrogenation and cracking increased. For example, at 648 K the formation of new products such as dimethylbenzene and hexane occurred. After 60 minutes the selectivity to methylcyclohexane over MoO₃ was 7.20% at 598 K increasing to 15.4% at 648 K. However, temperature did not affect the degree of hydrogenolysis over the MoO₃ catalyst since all products were oxygen free. Hydrogenolysis was found to be the primary reaction followed by the hydrogenation of toluene to saturated products.

MoO₃ was found to be more active than MoO₂ and MoS₂ for the HDO of 4MP (Table 1).

MoO₃ exhibited the lowest surface area and highest activation energy (118 kJ/mol) for HDO, compared to 109 kJ/mol on MoO₂.

Significance

MoO₂ and MoS₂, with molybdenum oxidation states of (IV), had similar surface areas, rate constants and selectivities for the HDO of 4MP. Both catalysts had the same degree of hydrogenolysis, but differed in hydrogenation selectivity - with MoS₂ having a higher selectivity for complete hydrogenation to m-cyclohexane. The Mo ligand had a minor effect on the activity of the HDO reaction, and a small effect on product selectivity. Overall, the oxidation state of the Mo played the most significant role in determining the activity and degree of hydrogenolysis.

The surface areas reported in Table 1 are those of the fresh catalysts. The surface area of MoO₃ increased from 0.3 m²/g to 3.5 m²/g after reaction at 598 K in H₂. At the reaction conditions full reduction of MoO₃ to MoO₂ or zero valent metal does not occur. During TPR, less than 1% reduction of MoO₃ occurred at 598 K but the catalyst's color changed from light green to dark blue (TPR), indicative of Mo oxidation states between (V) and (VI) [5]. The exterior phase of MoO₃ is likely reduced to a form of Mo_yO_x and Mo_yO_xH_z at the reaction conditions. Thus, it is suggested that this reduced exterior phase dispersed on MoO₃ performs the removal of oxygen from 4MP with high selectivity. The higher oxidation state (Mo(V) versus Mo(IV)) increased HDO activity, likely because Mo(V) is a strong electron acceptor for the oxygen of 4MP. Overall, both the Mo oxidation state and catalyst surface area play a role in the activity of the catalyst.

The data presented herein will also be compared to MoP catalysts, which have been shown to be active for HDO processes [6].

Table 1. 4MP HDO at 598 K and 4.14 MPa H₂.

Cat.	Surface Area (m ² /g)	k_{4MP} (mL.s ⁻¹ .mol _{Mo} ⁻¹)	After approximately 4 h.			
			X _{4MP} (%)	Toluene (%)	m-Cyclohexane (%)	4-m-Cyclohexene (%)
MoS ₂	4.2	0.292	26.4	71.1	10.3	5.7
MoO ₂	5.3	0.294	24.7	68.5	3.8	10.1
MoO ₃	0.3	1.26	70.7	59.0	14.4	6.6

References

1. Furimsky, E. *Appl. Catal. A* 199, 147 (2000).
2. Bunch, A., and Ozkan, U. *J. Catal. A* 206, 177 (2002).
3. Furimsky, E., Mikhlin, J., Jones, D., Adley, T., and Baikowitz, H. *Can. J. Chem. Eng.* 64, 982 (1986).
4. Matsuda, T., Hirata, Y., Uchijima, F., Itoh, H., and Takahashi, N. *Bull. Chem. Soc. Jpn.* 73, 1029 (2000).
5. Cotton, F., and Wilkinson, G. in "Advanced Inorganic Chemistry (A Comprehensive Text)" Edition 3, p. 947. Interscience Publishers, New York, 1972.
6. Clark, P., Wei, L., and Oyama, T. *J. Catal.* 200, 140 (2001).