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Research Paper

A study of the hydrodeoxygenation of anisole over Re-MoO_x/TiO_2 catalyst

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ABSTRACT

A well-characterized Re-MoO_x/TiO_2 catalyst was used to investigate the reaction sequence involved during the hydrodeoxygenation of anisole in a batch reactor by varying the initial anisole concentration in the reactant mixture (0.182–0.382 mol L^{-1} corresponding to 2.6–5.4 wt.%), the reaction temperature (250–325 °C) and hydrogen pressure (30–60 bar). The effects of these process variables on product selectivity, calculated at 10% anisole conversion, and reaction rate, estimated from the initial slope of anisole conversion vs. time, were discussed. The initial reaction rate was observed to increase to a maximum at anisole concentration of 0.282 mol L^{-1} and then decrease at higher concentrations. Mathematical modeling of the proposed reaction network revealed that the decreased activity at higher anisole concentration is related to diminished ability to cleave C—O bonds on phenol and cresols, probably due to increased surface coverage by the reactant on the oxophilic sites on the catalyst which limits access to surface reactive hydrogen for transformation. In regards to the influence of reaction temperature, high temperature favors the formation of cresols at the expense of benzene which was confirmed by the estimated apparent activation energy of the different pathways. On the other hand, the observed strong dependence of benzene/phenol ratio on H_2 pressure is attributed to increased availability of surface reactive hydrogen surface to aid in oxygen removal. Results from this study and the literature indicates that C—O bond breaking is preceded by either protonation of oxygen on anisole or by partial hydrogenation of the aromatic ring to lower the C—O scission barrier. Analysis of the conversion of intermediate compounds confirmed the reaction sequence and preferences during anisole HDO on Re-MoO_x/TiO_2 catalyst.

1. Introduction

Accelerated progress in catalysts research for hydrodeoxygenation (HDO) of biomass-derived compounds has been made within the last several years. A number of catalysts have been investigated for HDO, including metal sulfides, noble metals, transition metal carbides, phosphides and nitrides [1,2]. Many of the previous publications have highlighted the effectiveness of bifunctional catalysts, containing a balance of metal and acid sites, in HDO catalysis. There are reports of intriguing combinations of metallic functions (Pd, Pt, Ni, Ru, etc.) and acidic materials (H_3PO_4, HZSM-5, HY, HBEA, SO_4^{2-}/ZrO_2, Nafion) as examples of bifunctional catalysts for HDO of lignin-derived phenolic compounds (e.g. guaiacol, anisole, phenols, cresols, etc.) [3–14]. The metallic centers are responsible for hydrogen dissociation and hydrogenation, while the acid sites are required for adsorption of the substrates in addition to catalyzing intermediate reactions such as dehydration, hydrogenolysis, isomerization and hydrocracking reactions [5,10].

These findings have paved the way for exploring a wide range of metal/acid combinations. In that regard, recent studies have shown that synergistic effect between metal and partially reduced metal oxides (acid sites) give rise to bifunctional catalytic properties [15,16]. Echeandia et al. [15] concluded that the coexistence of Ni and WO_x species was responsible for the increased deoxygenation activity for phenol HDO. Similarly, Hong et al. [16] emphasized the importance of the cooperative function between Pd metal sites and Pd-WO_x acidic sites for the HDO of guaiacol. Deutsch and Shanks [17] demonstrated the bifunctionality of a $CuCr_2O_4 \cdot CuO$ catalyst in the HDO of a library of lignin derivatives in which Cu^0 constituted the hydrogenation and hydrogenolysis component and weakly acidic Cr_2O_3 catalyzed the dehydration and transalkylation reactions. Recently, we investigated a series of metal–metal oxide catalysts (i.e. Ga, Ni, Re and Co paired with MoO_x

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and VO_x) supported on TiO_2 for the HDO of anisole at 300 °C and 30 bar in a batch reactor [18]. The proposed reaction scheme was in agreement with literature [2] and involves three major pathways: (1) cleavage of the methoxy functionality ($O-CH_3$) to form phenol; (2) cleavage of aromatic carbon$-OCH_3$ bond to form benzene, and (3) methyl substitution (MT) into the aromatic nucleus to form cresols. Benzene is also produced as a secondary reaction, in addition to toluene, cyclohexanone, cyclohexene, cyclohexane and methylcyclohexane. The results found Re-MoO_x/TiO_2 to feature the highest selectivity towards aromatic hydrocarbons due to the oxophilicity of rhenium. In addition, it was found that equimolar proportions of Re and Mo led to a balance of specific sites needed to maximize selectivity to benzene and toluene. However, a detailed kinetic analysis of the HDO of anisole over this catalyst has not been established. The effect of reaction conditions, as well as the different reaction pathways, requires further investigation to provide insights on the hydrodeoxygenation ability of Re-MoO_x/TiO_2 catalyst and explore the parameters that govern selectivity.

A number of recent studies have focused on understanding the reaction sequence of mono- and bi-functional phenolic compounds on different catalysts [5,10,19]. For example, Saidi et al. [19] studied anisole HDO reaction over Pt/Al_2O_3 at 300–400 °C and 8–14 bar and estimated the rate constants and activation energies for the primary steps in the reaction network. The authors fitted the primary reactions with a first-order approximation which showed phenol as the principal product; additionally, other primary reactions observed include hydrogenolysis to benzene and transalkylation to form cresol. Zhao et al. [10] investigated the detailed kinetics of the individual reaction steps of phenol HDO in aqueous medium over Ni supported on HZSM-5 or Al_2O_3-HZSM-5, and found the overall rate to be controlled by phenol hydrogenation to cyclohexanone. Gonçalves et al. [20] used kinetic modeling on the proposed reaction network to highlight the effect of the methyl group in cresol isomers over Ni_2P/SiO_2 between 250 and 340 °C and under 16–32 bar H_2 pressure. Khromova et al. [21] described the experimental dependence of anisole conversion over NiCu-SiO_2 catalysts at 280 °C and 60 bar by first-order kinetics with respect to anisole and the products. The authors proposed three pathways based on the results of kinetic modeling, comprising direct conversion of anisole into benzene (HDO route) or hydrogenation of aromatic ring of anisole to form methoxycyclohexane and cyclohexanol. However, to the best of our knowledge, there are no studies in the literature focusing on reaction network analysis of the conversion of lignin oxygenate on catalysts consisting of metal and metal oxide components. In our viewpoint, the promising results of the Re-MoO_x/TiO_2 catalyst provide a rationale to study the influence of processing conditions and the different routes of anisole HDO to add valuable insights to HDO catalysis, particularly since reducible ReO_x containing catalysts have been demonstrated to be effective in cleaving C$-$O bonds in a variety of lignocellulosic-derived compounds [22–27]. Therefore, the objective of this contribution is to carry out experiments on the effect of anisole concentration, reaction temperature and H_2 pressure to better understand the reaction sequence of this important bio-oil model compound. Experiments on intermediate compounds from anisole conversion were used to explore the different reaction pathways. Based on the experimental results and reaction network analysis, performed by fitting the transformation of anisole and products by a series of ordinary differential equations, it is possible to indicate the reaction trajectory which provides further insights on the catalytic behavior of Re-MoO_x/TiO_2 catalyst.

2. Experimental

2.1. Reagents

Anatase titanium (IV) oxide (TiO_2, $S_{BET} = 157\ m^2\ g^{-1}$) was purchased from Alfa Aesar and used as support without any pretreatment. Ammonium molybdate tetrahydrate [≥99%, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$], anisole (99%), phenol (99%), dodecane (99%), benzene (99.5%), *o*-cresol (99%), toluene (99.9%), cyclohexane (99.9%), and isopropanol (99.5%) were obtained from Merck. Ammonium perrhenate (≥99%, NH_4ReO_4), hexadecane (99%) and cyclohexanone (99%) were supplied by Sigma–Aldrich. The gases used were H_2 (99.995%, Linde), N_2 (99.995%, Linde), 5% O_2/N_2 (certified mixture grade, Linde) and synthetic air (Linde). All chemicals in this work were used without further purification.

2.2. Catalyst preparation and characterization

The Re-MoO_x/TiO_2 catalyst was prepared by sequential impregnation of TiO_2 (ground and sieved to obtain 100–140 μm particle size) with aqueous solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, followed by impregnation with aqueous solution of NH_4ReO_4. The catalyst was prepared to obtain Re and Mo nominal loadings of 10.8 wt.% and 5.6 wt.%, corresponding to an equimolar loading of 0.50 $mmol\ g_{cat}^{-1}$. After the first impregnation, the sample was kept at room temperature for 24 h, dried at 110 °C for 15 h and calcined at 500 °C (ramp rate of 2 °C min^{-1}) for 4 h. The second impregnation with the Re precursor salt was followed by the same drying procedure but calcination was at 300 °C for 0.5 h.

The calcined sample was reduced *ex situ*, in a quartz reactor tube placed inside an electrical furnace, in H_2 (60 mL min^{-1}) from 25 to 500 °C at 10 °C min^{-1}, and kept at 500 °C for 3 h. The sample was cooled to ambient temperature in N_2 (60 mL min^{-1}), passivated in 5% O_2/N_2 (30 mL min^{-1}) for 1 h with the reactor immersed in an isopropanol/liquid nitrogen slurry bath, and then for 1.5 h at ambient temperature.

The catalyst was characterized by N_2 physisorption at 77 K, atomic absorption spectroscopy and inductively coupled plasma mass spectrometry to determine the Mo and Re content, respectively, X-ray diffraction with a Ni-filtered CuKα_1 radiation ($\lambda = 1.5418$ Å), H_2-temperature programmed reduction, temperature programmed desorption of ammonia (TPD-NH_3), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Details of the catalyst characterization measurements can be found in our previous study [18].

2.3. Reaction measurements

The conversion of anisole and its intermediates were evaluated in a stainless steel 100 mL Parr batch reactor (Parr Series 4590) using dodecane as solvent and hexadecane as an internal standard. About 200 mg of catalyst was added into the reactor containing appropriate amount of anisole (1.6–3.5 mL), 80 mL of dodecane and 700 μL of hexadecane. The reactor was sealed and purged with N_2 flow for 10 min to evacuate air from the system, and then charged with 1 bar of nitrogen to fill dead volume of the reactor. Then, the reactant mixture was heated to 300 °C while stirring at 700 rpm, and charged with hydrogen to 50 bar. The start of the reaction was assumed to be when the reaction temperature was reached and H_2 was introduced into the reactor. The reaction was punctuated by the addition of hydrogen to maintain the pressure for the entire duration of the experiment. Aliquot of around 0.5 mL was periodically withdrawn for 240 min and analyzed by a DANI Master gas chromatography with an Elite-1 column (Perkin Elmer, 30 m × 0.32 mm, film thickness of 0.25 μm) and flame ionization detector (FID). The products were identified by their column retention time in comparison with available standards.

The effect of reaction temperature (250–325 °C) was determined using an anisole concentration of 0.232 mol L^{-1} and a total pressure of 50 bar, while the effect of hydrogen pressure (30–60 bar) was investigated at 300 °C and 0.232 mol L^{-1} anisole concentration. The reaction lasted for 4 h, while shorter runs of 1 h were made for the conversion of the intermediate products which was studied at 300 °C and 50 bar using the same procedure described.

The catalytic activity was expressed by the initial reaction rate r_s ($mol\ g^{-1}\ s^{-1}$), calculated from the initial slope of the conversion vs.