Anisole hydrodeoxygenation over supported CoMo catalysts: effect of Co/Mo ratio and support on catalyst stability and activity

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1. Introduction

Catalytic hydrodeoxygenation (HDO) is one of the most promising routes to upgrade pyrolysis oils for producing liquid transportation fuels[1]. The complexity of fast pyrolysis oil has prompted the use of model compounds such as phenolics, furans, ethers, acids etc. to study the intricacies of HDO behavior. Anisole, because of its methoxy group, has already been widely investigated as a model compound for lignin derived bio-oil[2]. The low sulfur content in bio-oil renders the use of traditional sulfided catalysts such as NiMoS and CoMoS less interesting as they require a tailored amount of sulfur to maintain their activity and selectivity and, hence, lead to sulfur contamination in the end products. To mitigate this issue, non sulfided transition metal (Ni, Co, Mo) catalysts on various supports have been investigated for hydrotreatment of bio-oil model compounds[3-4]. Yet, significant challenges remain in improving the catalyst activity, stability, and HDO selectivity. Our previous work on MoO_3/ZrO_2 catalysts showcased HDO selectivity of up to 50% with a continuous decrease in catalyst activity over 100 h time on stream (TOS)[5-6]. Our present work explores the details of anisole HDO reaction pathways with the addition of Co to the Mo catalysts and testing in their non-sulphided form through systematic intrinsic kinetic experimentation. Through this, we aim to achieve a stable catalytic active phase with increased HDO selectivity in comparison to MoO_3 catalysts. The catalysts performance is interpreted in terms of catalyst properties such as active phase dispersion, reducibility, crystallite size, and metal-support interactions. Present study serves as a significant step forward for the development of selective and stable catalysts for the HDO reaction, which is fundamental for the design of an optimal catalyst for catalytic upgrading of bio-oil that aims the production of liquid biofuels.

2. Experimental

A series of Al_2O_3 and ZrO_2 supported CoMo catalysts were prepared with varying Co/Mo ratio (0.02, 0.08, 0.25, 0.58, and 1.07) while keeping the Mo loading between 8.3 – 11.2 wt%. A sequential incipient wetness impregnation (with Mo being introduced first) method using aqueous solutions of the corresponding precursor salts was employed during the synthesis procedure. Material physicochemical characteristics were evaluated through ICP-OES, BET, (in-situ) XRD, H_2-TPR, NH_3-TPD, H_2-chemisorption, XPS, (S)TEM and EDX techniques. The performance of these CoMo catalysts was tested for anisole HDO at gas phase conditions in a fixed bed tubular reactor in plug flow regime. A high-throughput kinetics screening set-up (HTK-S)[7] comprising 16 plug flow reactors with an internal diameter of 0.00211 m and a length of 0.85 m was used for the acquisition of intrinsic kinetic data. The product stream is analyzed with the help of an on-line gas injection to a DHA (Detailed Hydrocarbon Analyzer) TraceGC1310 equipped with a flame ionization detector (FID).

3. Results and discussion

Figure 1 displays the anisole conversion and product selectivity for $CoMo/Al_2O_3$, $CoMo/ZrO_2$, MoO_3/ZrO_2, and MoO_3/Al_2O_3 catalysts during a stability test (TOS of 50 h). Al_2O_3 supported catalysts displayed higher anisole conversions compared to ZrO_2 ones at the investigated operating conditions. Addition of Co improved catalyst stability as can be observed through Figure 1. Figure 2 showcases the proposed reaction pathways for supported CoMo catalysts in the present study. $CoMo/Al_2O_3$ catalysts mainly promote the transalkylation and isomerization reactions whereas, ZrO_2 supported ones promote hydrodeoxygenation and transalkylation reactions. Catalyst reducibility effect on performance was studied by varying the temperature to reduce the catalyst prior to the reaction. An increase in catalyst reduction temperature from 673 to 773 K resulted in an increase in benzene selectivity, yet a decrease in anisole conversion for ZrO_2 supported catalysts, whereas, Al_2O_3 supported catalyst exhibited a decrease in benzene selectivity while having no significant drop in anisole conversion with TOS.

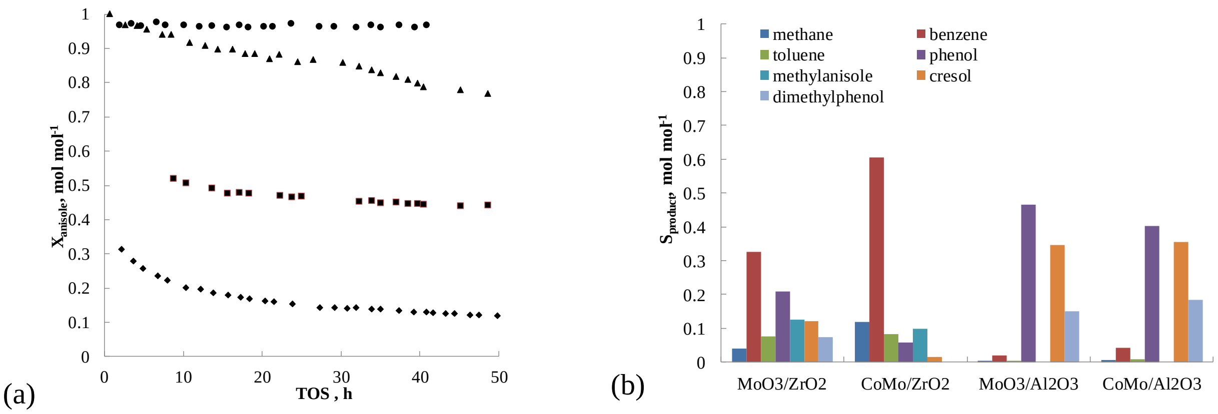

Figure 1. (a) Stability experiment with (●) CoMo/Al$_2$O$_3$, (■) CoMo/ZrO$_2$, (◆) MoO$_3$/ZrO$_2$ [5], and (▲) MoO$_3$/Al$_2$O$_3$ catalysts at T = 613 K, P$_T$ = 0.5 MPa, H$_2$/anisole = 50 mol mol^{-1}, space-time = 126 kg$_{cat}$ s mol^{-1}$_{anisole}$. (b) Product selectivity at TOS = 40 h. Co/Mo = 1.07 for both CoMo catalysts, Mo wt.% = 11.2 for all the catalysts.

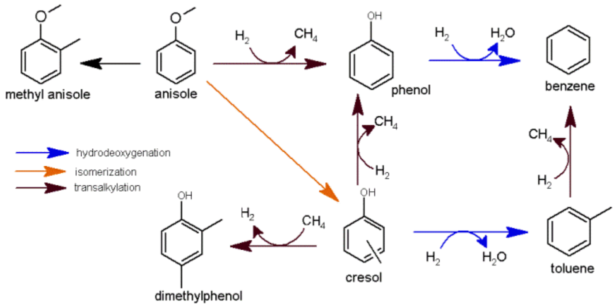

Figure 2. Proposed anisole reaction pathways over CoMo catalysts

Further reaction pathway elucidation is done with the use of intrinsic kinetic measurements varying space time (50 – 300 kg$_{cat}$ s mol^{-1}), temperature (523 - 623 K) and H$_2$/anisole inlet molar ratio (50-150 mol mol^{-1}) with best performing catalysts. Catalyst deactivation causes will be explored through characterization (O$_2$-TPO, XRD, XPS, (S)TEM and EDX) of spent catalyst samples. Increase in Co content affected the reducibility of the material through mixed oxide (CoMoO$_4$) formation. The structural characteristics of the reduced catalysts, such as metal-metal oxide combination resulted in a high HDO activity compared to the MoO$_3$ catalysts in our previous study[5-6], Catalyst activity-structure correlations drawn from present study can serve significantly in guiding the synthesis of next generation catalysts with better catalyst stability and activity during anisole HDO.

4. Conclusions

The role of Co/Mo ratio and the support on catalysts stability as well as HDO activity observed during an extensive experimental campaign are correlated to key properties such as active site dispersion, reducibility, crystallite size, and metal-support interaction through H$_2$-TPR, (in-situ) XRD, H$_2$-chemisorption, XPS, (S)TEM-EDX analyses of the reduced as well as spent catalysts. Supported CoMo catalysts exhibit higher HDO activity as well as stability than their MoO$_3$ counterparts at the investigated operating conditions during anisole HDO over 50 h TOS.

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