Supported Molybdenum Oxide catalysts for Hydrodeoxygenation (HDO) of Lignin-Derived Model Compounds

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Introduction

Lignocellulosic biomass is a renewable source of carbon for production of fuels and chemicals. Bio-oil obtained from biomass pyrolysis cannot be directly used as a fuel without upgrading. Upgrading lignin-derived phenolic compounds is one of the biggest challenges in bio-oil upgrading. Key challenges include obtaining high hydrocarbon yield, with low H2 consumption[1]. Recently, MoO3 has been shown to be earth-abundant, selective, and stable catalysts for the HDO of various biomass-derived oxygenates including lignin-derived model compounds[1, 2]. Local structure of the dispersed state of MoO3 species depend on the support, and influences its reactivity[3]. In this work, we report the reactivity and stability of MoO3 supported on different metal oxides catalysts for HDO of lignin-derived model compounds.

Materials and Methods

m-cresol (99%, Sigma-Aldrich) was used as a feed. H2 (99.999%, Airgas) was used as reactant gas. MoO3 (>99.5%), nTiO2 (21nm, ≥ 99.5%), nSiO2 (5-15 nm, 99.5%), were purchased from Sigma-Aldrich. γ-Al2O3 (1/8” pellet, Alfa Aesar) was ground and sieved, and particles < 200 mesh were used as support. nZrO2 and nCeO2 nanoparticles were synthesized using previously reported method[4]. 10 wt% MoO3 catalysts were synthesized using incipient wetness impregnation method, using aqueous (NH4)3MoO4.H2O (99%, Alfa Aesar) solution as precursor.

Catalytic testing experiments were conducted in vapor-phase packed-bed flow reactor. The catalyst (25 mg eq. MoO3) was mixed with an inert, (α-Al2O3) and loaded in the middle of a SS reactor (3/8”) mounted inside a furnace (ATS, Series 3210). Temperature (320°C) was controlled by a thermocouple (Omega, TY36-CAXL-116u) connected to a temperature controller (Digi-Sense, 68900-10). Liquid feed (200 μl h-1) introduced via syringe pump (Harvard Apparatus, 700300S) is vaporized and mixed with H2 gas (70 ml min-1) at inlet of reactor. The products are analyzed by online GC-FID (Agilent 7890A) fitted with a DB-5 column, downstream of the reactor.

O2 chemisorption and BET surface area measurements have been performed using Quantachrome Autosorb IQ automated gas sorption system.

Results and Discussion

Figure 1(a) shows the reactivity of supported MoO3 catalysts. MoO3/nZrO2, MoO3/γAl2O3, and MoO3/nTiO2 show the highest reactivity for the HDO of m-cresol to toluene. The dispersion of molybdenum on support surface is obtained by O2 chemisorption as shown in Table 1. The catalysts are surface reduced by treating it with H2 at 350°C for 2 h, followed by adsorption of O2 at the same temperature. The dispersion of molybdenum on the catalyst support seems to be the highest on TiO2, and ZrO2 supports. Conversion for MoO3/γAl2O3 is found to be lower, probably due to lower dispersion (not shown here).

| Table 1. O2 chemisorption and BET surface area measurement for supported MoO3 catalysts. |
| Catalysts (10 wt% loading) | BET surface area (m2/gm) | Metal surface area (m2/gm) | O2 uptake (μmol/gm) | Surface coverage (%) | Metal dispersion (%) |
| MoO3/nZrO2 | 117.3 | 12.1 | 137.9 | 10.3 | 39.7 |
| MoO3/nTiO2 | 54.1 | 21.5 | 245.0 | 39.8 | 70.6 |
| MoO3/nSiO2 | 268.8 | 8.6 | 98.3 | 3.2 | 28.3 |
| MoO3/γAl2O3 | 223.3 | 3.8 | 43.1 | 1.7 | 12.4 |
| MoO3/nCeO2 | 29.7 | 11.6 | 131 | 38.9 | 37.7 |

At this loading, molybdenum species are found to be largely present as polymolybdate species by Raman spectroscopy (not shown here). The temperature-programed reduction (TPR) as shown in Figure 1(b) shows better redox behavior for MoO3/nZrO2 MoO3/γAl2O3 and MoO3/nTiO2 catalysts. Redox behavior is critical for the proposed reverse Mars van Krevelen mechanism for HDO on MoO3[2]. Hence, the increased activity of MoO3/nTiO2 and MoO3/nZrO2 may be attributed to combined effects of better dispersion, and redox behavior due to metal-support interaction.

Significance

This work is a significant step towards designing effective catalytic systems for bio-oil upgrading. Supported MoO3 have been shown to be effective catalysts for HDO of lignin-derived model compounds. MoO3/nTiO2 and MoO3/nZrO2 are effective, and robust, towards HDO of phenolic compounds, as compared to bulk MoO3.

References