Composition Effects on the Structure and Methanol Transformation Reactivity of Porous Au-WO_3 Catalysts

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Abstract

The catalytic transformation of methanol (MeOH) under aerobic conditions is an important reaction used to probe the acidic and redox nature of metal oxide catalyst active sites. Product distribution analysis yields information on the contribution of individual components in a mixed oxide catalyst during the reaction. Dimethyl ether (DME) forms as a result of acid-catalyzed MeOH dehydration, while redox-active sites yield the oxidation product, formaldehyde (HCHO). We have prepared high surface-area porous tungsten oxide (WO_3) catalysts with abundant surface acid sites that are highly selective for DME. We have modified these WO_3 catalysts with gold nanoparticles (Au NPs) to study the effects of composition on MeOH transformation activity and selectivity. Methanol transformation catalysts composed of both Au and WO_3 have not been widely studied. A sonochemical method was used to deposit Au NPs on the surface of porous SiO_2 (Au-SiO_2) followed by incorporation of WO_3 (Au-SiO_2-WO_3), and then finally selectively etching of SiO_2 to yield Au-WO_3 catalysts. Complete characterization of the porous catalysts was carried out using powder X-ray diffractometry (XRD), electron microscopy, infrared spectroscopy, and N_2 physisorption in order to study the effect of Au NP deposition on the WO_3 structure. In addition, changes in surface acid sites were probed by ammonia temperature-programmed desorption (NH_3-TPD). Finally, catalytic MeOH transformation tests were conducted on catalysts of various compositions (Au-SiO_2-WO_3, Au-WO_3, SiO_2-WO_3, and WO_3). A comparison of the MeOH transformation activity is made between Au-doped and non-doped catalysts. We also present a discussion of NH_3-TPD data and correlate these results to the observed product distribution during MeOH transformation tests. Pure WO_3 catalysts are highly selective for DME at all conversions, whereas Au-WO_3 yields HCHO in addition to DME. Gold NPs increase the activity of WO_3 catalysts and introduce redox-active sites on the surface.