Heterogenous Propylene Metathesis over Molybdenum Silicate Microspheres with Dispersed MoO_x Sites

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Olefin metathesis is a versatile strategy that finds use in numerous applications, from the synthesis of fine chemicals to the large-scale production of petroleum commodities. Herein, we report on the synthesis of a series of amorphous and porous molybdenum silicate microspheres (Mo-SiO_2) with varying Mo contents (1.6 to 11 wt.%) and investigate their reactivity using heterogeneous propylene metathesis as the probe reaction. The Mo-SiO_2 microspheres were synthesized by non-aqueous condensation of a hybrid molybdenum biphenyldicarboxylate-based precursor solution with (3-Aminopropyl)triethoxysilane. Characterizations of the synthesized microspheres were performed with XPS, ^{29}Si solid-state NMR, SEM, and nitrogen adsorption isotherms. Results from in-situ DRUV-Vis and ToF-SIMS revealed that the microspheres comprised mainly atomically dispersed MoO_x species. In-situ FTIR of pyridine adsorption at 150 °C revealed Lewis acid sites on all microspheres, and pyridinium ions from Bronsted acid sites only on Mo-SiO_2 with Mo content $\geq$ 6.7 wt.%. H_2-TPD revealed enhanced reducibility of the Mo-SiO_2 microspheres with increasing Mo content. Remarkably, the microspheres with low Mo content (1.5-3.6 wt.%) exhibited almost two orders of magnitude higher steady-state propylene metathesis rates at 200 °C compared to conventional silica-supported MoO_x catalysts prepared via incipient wetness impregnation, resulting in the highest molybdenum content normalized site time yields of 0.11 s^{-1}. However, the metathesis reactivity of Mo-SiO_2 (catalyst mass normalized rates and Mo content normalized site time yields) starts to decrease when Mo content is higher than 4 wt.%. We ascribe these decreases in reactivity primarily to the excessive reducibility of the Mo-SiO_2 microsphere with high Mo content, leading to the formation of surface acetate that obstructs the surface MoO_2 active site. These findings suggest Mo-SiO_2 microspheres with high olefin metathesis reactivity as promising potential catalysts for industrial applications and provide insights into the correlation between Bronsted acidity, reducibility, and metathesis reactivity of the catalysts for advanced catalyst design.