

Influence of catalyst support structure on ethene/decene metathesis and coke formation over WO_3/SiO_2 catalyst

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Abstract: 8wt% WO_3/SiO_2 metathesis (disproportionation) catalysts with different pore structures were prepared by the incipient-wetness-impregnation method. The as-synthesized catalysts were characterized by N_2 adsorption-desorption, scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-visible diffuse reflectance spectroscopy (DRS) and scanning transmission electron microscopy–high-angle annular dark field (STEM HAADF). The results of STEM HAADF showed that WO_3 species were not uniformly distributed on the SiO_2 support. The experimental results of 8wt% WO_3/SiO_2 performance in ethene/decene metathesis revealed that the catalytic effect of 8wt% WO_3/SiO_2 catalyst and coke formation over it were closely related to the support pore structure: The 8wt% WO_3/SiO_2 catalyst with a more complicated pore structure showed better catalytic performance but the coke deposition rate was also faster.

Key words: Metathesis, WO_3/SiO_2 catalysts, pore structure, coke formation

1 Introduction

The catalyst used for olefin metathesis is comprised of at least one transition metal such as tungsten, rhenium, molybdenum, ruthenium and osmium, and the technology of alkene metathesis to produce propene has been improved significantly in recent decades (Shell Oil Company, 1992a, 1993b). Most catalysts used for aliphatic olefins metathesis are rhenium, molybdenum or tungsten oxide loaded on a porous inorganic support (Mol, 2004; van Schalkwyk et al, 2003; Zhao et al, 2009). Among them, WO_3/SiO_2 catalyst has drawn a lot of attention because of its insensitivity to trace amount of poisons (Hua et al, 2011a; Spamer et al, 2003).

For tungsten-based catalysts, a lot of research, aimed at calcination time, moist atmosphere performance, preparation procedures, tungsten loadings and support porous structure, has been conducted for investigating their metathesis catalytic performance (Huang et al, 2007a; 2007b; Liu et al, 2009; Hu et al, 2006; Wang et al, 2003). It is known that coke formation over WO_3/SiO_2 catalysts is serious because of high metathesis temperature (350–500 °C) (Hua et al, 2011b). Moodley et al (2007) have studied coke formation over WO_3/SiO_2 catalyst in the metathesis of 1-octene and 1-heptene to longer chain internal alkenes and the results indicated that heavier internal

alkene products coked more rapidly than 1-octene. By the use of energy-filtered transmission electron microscopy (EFTEM), they found that WO_3/SiO_2 catalyst was still active even at high coke level because the coke was mainly formed over the supports rather than the active tungsten species.

To further understand the coke formation over WO_3/SiO_2 catalysts, we characterized 8wt% WO_3/SiO_2 metathesis catalysts with different pore structures by XRD, UV-Vis DRS, SEM and scanning transmission electron microscopy–high-angle annular dark field (STEM HAADF), and their catalytic performance in ethene/decene metathesis was evaluated, then the coking behavior of the catalyst was investigated.

2 Experimental

2.1 Catalyst preparation

Commercial silica gel (CSG) were provided by Qingdao Haiyang Co. Ltd, China, and a support (denoted as S40) was prepared by evaporation-driven self-assembly of 40 nm monodisperse SiO_2 spheres in our work. The two SiO_2 supports were separately impregnated with ammonium metatungstate solution, dried at 50 °C for 6 h, then at 100 °C for 2 h, finally calcined in a muffle. The temperature of the muffle was raised to 550 °C at 3 °C/min and kept for 5 h. The 8wt% WO_3/SiO_2 catalysts were thus obtained.

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