ENHANCED METATHESIS OF ETHYLENE AND 2-BUTENE ON TUNGSTEN INCORPORATED ORDERED MESOPOROUS SILICATES

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Abstract

Tungsten-incorporated 3D mesoporous silicates, W-KIT-6 catalyst, perform better than WO_3/SiO_2 catalysts towards the methathesis of ethylene and 2-butene into propene at 450 °C. All W-mesoporous catalysts exhibit steady activity and stability during 7 h runs in a fixed-bed reactor. In addition, the propene yield varies with the catalyst total acidity. UV/Vis DRS spectra revealed that tetrahedrally and octahedrally-coordinated W-species are the active species. The superior performance of the W-incorporated mesoporous catalysts is attributed to the better dispersion of active tungsten species as confirmed by UV/Vis spectra.

Keywords

Metathesis, ethylene, 2-butene, tungsten, mesoporous silicates

Introduction

In the United States, the supply of natural gas liquids (NGLs) has increased dramatically as a collateral product of shale gas extraction. Oversupply of ethylene and shortage of propene are expected as a result of increased NGLs supply and decreased naphtha availability (Foster, 2013). Therefore, synthesizing propene from abundant and inexpensive ethylene via olefin metathesis is promising. WO_3/SiO_2 catalyst is typically used for industrial metathesis reaction of ethylene and 1-butene to propene at pressure of 30-35 bar (Mol, 2004). Recently, it was reported that tungsten incorporated into mesoporous silicates (such as the W-KIT-6 catalyst developed at the CEBC) displayed superior activity compared to WO_3/SiO_2 (Hu et al., 2013). Based on these promising results, we are systematically exploring a low-pressure metathesis technology with W-incorporated mesoporous silicates W-KIT-6.

Experimental, Results and Discussion

W-KIT-6 (Ramanathan et al., 2012) catalyst is prepared as reported in the referenced studies. WO_3/SiO_2 and WO_3/Si-KIT-6 catalysts were prepared by wet impregnation of the silica supports (fumed SiO_2 and Si-KIT-6). The catalytic performances of the W-catalysts for metathesis of ethylene and 2-butene into propene were evaluated in a continuous flow fixed-bed Parr type reactor with i.d. = 9.4 mm. Reaction conditions are listed in Figure 1 caption.

Figure 1 compares the propene yields of the two WO_3-impregnated catalysts, WO_3/SiO_2 (7.4) and WO_3/Si-KIT-6 (7.6) (The number in the bracket is the weight percent of tungsten in these catalysts). The yields are similar (28.3-33.2 %) and stable after a 1.5 h line-out period.

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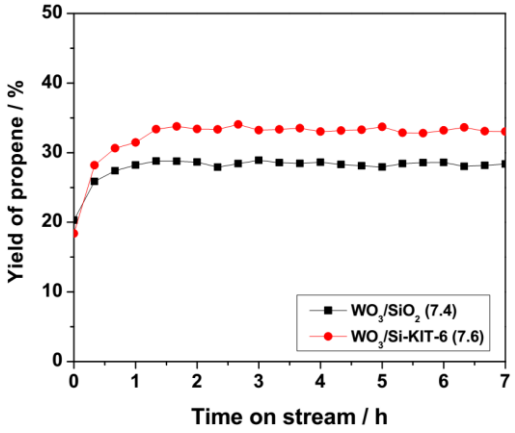

Figure 1. Propene yield as a function of time on stream of two WO_3-impregnated catalysts, WO_3/SiO_2 (7.4) and WO_3/Si-KIT-6 (7.6) at 450 ℃, 1 atm, WHSV (ethylene and 2-butene) = 2.0 h^{-1}, n(ethylene)/n(2-butene) = 3/1.

Figure 2 shows the propene yield of the W-incorporated mesoporous silicates, W-KIT-6. The steady propene yield increases as the tungsten loading increased from 2.8 wt% to 5.9 wt%, then decreased with further increase in the tungsten loading from 5.9 wt% to 13.7 wt%. The maximum propene yield ~46% (averaged value of propene yield between 3 to 7 h) was achieved at 5.9 wt% tungsten loading. In other words, the propene yield varies with the total acidity (right Y-axis in Figure 2).

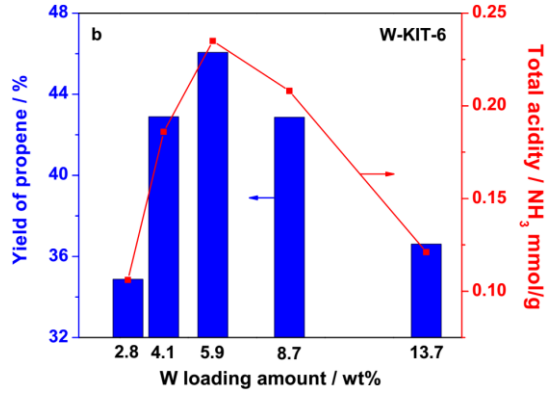

Figure 2. Propene yield and catalyst total acidity as a function of tungsten loading amount on W-KIT-6 catalysts.

Figure 3 shows the UV/Vis spectra of fresh W-KIT-6 catalysts. The spectra indicate that three surface species are formed: 1) tetrahedral tungsten species at 225 nm; 2) octahedral polytungstate species at 262 nm; 3) bulk WO_3 species at 400 nm. When the tungsten loading was decreased from 24.4 wt% to 11.7 wt%, the peak intensity of bulk WO_3 decreases, however, the yield of propene increases (Figure 2). This indicates that bulk WO_3 species are less active. The fact that a control experiment with bulk WO_3 shows no metathesis activity supports this hypothesis. The relative intensities of the bands at 225 and 262 nm on the various catalysts track the propene yield on these catalysts (Figure 2), indicating that the tungsten species with tetrahedral and octahedral configurations are the active species.

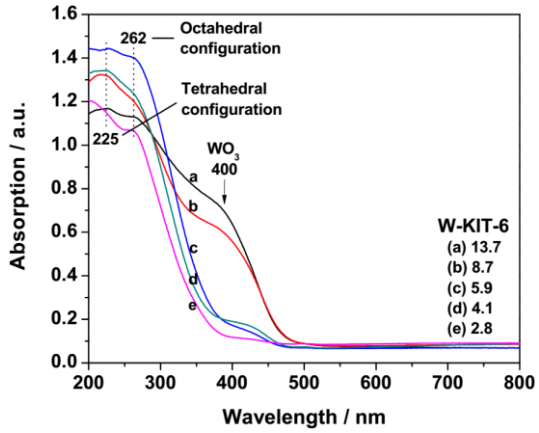

Figure 3. UV/Vis DRS patterns of fresh W-KIT-6 catalysts with different tungsten loading, (a) 13.7 wt%, (b) 8.7 wt%, (c) 5.9 wt%, (d) 4.1 wt%, and (e) 2.8 wt%, respectively.

Conclusions/Outlook

W-incorporated mesoporous silicates, W-KIT-6, show better performance than WO_3-impregnated SiO_2 catalysts towards the methathesis of ethylene and 2-butene into propene at 450 °C. UV/Vis DRS spectra indicate that tetrahedrally and octahedrally-coordinated W-species are the active species. Further optimization of catalyst synthesis method and reaction temperature to maximize propene yield and catalyst stability, as well as mechanistic insights from solid-state NMR and EPR studies will be presented.

References

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