Comparative studies of mesoporous SBA-15 supported tungsten oxide and rhenium oxide for 2-butanol dehydration

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Introduction

Highly dispersed tungsten oxides supported on mesoporous silica (SBA-15), prepared by a novel ALD (atomic layer deposition) method, have been reported to be very efficient for 2-butanol dehydration in our previous work [1]. Oxides of rhenium, which is a neighbor of tungsten in the periodic table, may also be of interest for this catalytic reaction. For this reason, in this work a comparative study has been performed of the dehydration of 2-butanol over SBA-15 supported WO_3 and ReO_3. Our results show that these two types of catalysts displayed significantly different performance with respect to catalytic activity, selectivity and stability for this reaction.

Materials and Methods

The supported tungsten oxide and rhenium oxide catalysts were prepared by a solution ALD method [1-2] onto SBA-15 supports, materials with a high surface area of ~860m^2/g, and an average pore size of 7nm after calcination at 500°C for 4h. The as-prepared supported oxide catalysts were calcined at 400°C for 1h. The composition of the catalysts was typically 30 wt% oxide on the SBA-15 support. The catalytic behavior for 2-butanol dehydration was measured in a quartz flow reactor at atmospheric pressure. The experiments were run in long-term isothermal mode to reach steady-state. The reaction was conducted at 105°C on WO_3/SBA-15 while temperatures as low as 50-70°C were used to examine the activities on ReO_3/SBA-15, in addition to experiments at 105°C. The catalytic performance of the catalysts was evaluated by reaction rates (TOF) and selectivity to products (1-, trans-2-, cis-2-butene) obtained at various conversion levels. The dispersion and chemical states of both supported metal oxides were characterized by HRTEM, XRD and UV-VIS (DR). A comparison between fresh and spent samples was made to investigate any structural change induced by reaction. Further, TPO was performed to elucidate C-deposition on the used catalysts, and solid state NMR was carried out to identify the nature of the deposited species.

Results and Discussion

Fig. 1 shows the activity results for 2-butanol dehydration over WO_3/SBA-15 and ReO_3/SBA-15. As can be seen, ReO_3/SBA-15 exhibits nearly 100% initial conversion of 2-butanol at 105°C and a flow rate of 200ml/min, while the conversion was below 20% for WO_3/SBA-15 under the same reaction conditions. Clearly, the activity of ReO_3/SBA-15 is much higher than that of WO_3/SBA-15, and it was thus necessary to decrease the reaction temperature to 50°C so that a representative TOF on the ReO_3/SBA-15 catalyst could be measured, as shown in Fig. 2(a). Besides the activity difference, these two catalysts also exhibit very different selectivities to butene (1-, trans-2-, cis-2-). As shown in Fig. 2(b), the trans/cis ratio is ~0.8 for WO_3/SBA-15, while a slightly higher value of ~1.0 was observed for ReO_3/SBA-15. This difference could suggest that different reaction mechanisms may exist for these two catalysts.

In addition, a much faster and more severe deactivation was observed for ReO_3/SBA-15, in comparison to WO_3/SBA-15, as shown in Fig.1. Severe sintering of rhenium oxide during reaction was a major factor for deactivation as evidenced by TEM analysis on both fresh and spent ReO_3/SBA-15 catalysts. TPO of spent ReO_3/SBA-15 catalysts also revealed the deposition of C-containing species. In contrast, neither phenomenon was observed for WO_3/SBA-15. Thus, we attribute the sintering and C-deposition processes as the two deactivation factors on ReO_3/SBA-15 in 2-butanol dehydration.

The above activity and stability features exhibited by ReO_3/SBA-15 and WO_3/SBA-15 are being further probed by complementary structural characterization studies. Activity regeneration, and the effect of gas feed composition such as water on deactivation is also being examined.

Significance

This is the first report on supported rhenium oxide as a potentially active dehydration catalyst. Although highly active, further insight on the understanding of deactivation of ReO_3/SBA-15 is needed, to suppress the observed rapid deactivation for this catalyst.

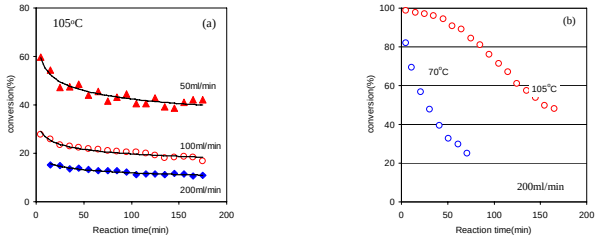

Figure 1. Conversion of 2-butanol with time during 2-butanol dehydration over (a) WO_3/SBA-15, and (b) ReO_3/SBA-15. Catalyst: 20mg; feed gas: 0.5% 2-butanol-He.

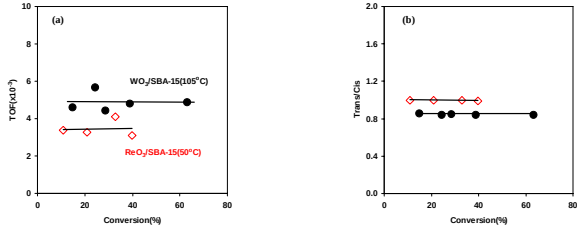

Figure 2. Activity and selectivity of 2-butanol dehydration over WO_3/SBA-15 (105°C) and ReO_3/SBA-15 (50°C): (a)TOF; (b) trans/cis 2-butene ratio.

References

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2. J. E. Herrera, J. H. Kwak, J.Z. Hu, Y. Wang and C. H.F. Peden, *Appl. Catal. A* 300 (2006) 109.