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Optimizing activity of tungsten oxides for 1-butene metathesis by depositing silica on γ-alumina support

Na Liu[1], *Shilei Ding*, *Yuming Cui*, *Nianhua Xue**, *Luming Peng*,
Xuefeng Guo, *Weiping Ding**

Key Lab of Mesoscopic Chemistry, The School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ABSTRACT

A series of catalysts made of tungsten oxide loaded on SiO_2, γ-Al_2O_3, SiO_2–Al_2O_3 and silica deposited γ-alumina are tested for 1-butene metathesis. Among these catalysts, the catalyst $6W/20SiO_2/Al_2O_3$ gives the highest activity for 1-butene metathesis reaction with 1-butene conversion up to 71 mol% and the yield of propene up to 21 mol%. The excellent catalytic activity is related to the moderate dispersion of tungsten oxide and the suitable acidity of the support. The dispersion of WO_x species and the acidity of supports were studied by characterization of XRD, Raman spectra, UV–vis, H_2-TPR and NH_3-TPD in detail. The surface properties of silica modified γ-alumina leads to the moderate aggregation of supported tungsten oxide, which appears to be more effective for 1-butene metathesis at the low temperature of 453 K. Optimized activity was realized by tuning the dispersion of tungsten species on silica deposited alumina.

Keywords: 1-Butene; Metathesis; Silica modified γ-Al_2O_3; Tungsten oxide

1. Introduction

Olefin metathesis has been the one of the very few fundamentally novel organic reactions discovered in the last 40 years (Ivin and Mol, 1997). A variety of transition metal compounds catalyze metathesis reaction of alkenes and the most successful ones are based on W, Mo and Re in high oxidation states (Imamoglu et al., 1989; Heckelsb et al., 1968; Grunert et al., 1989; Hu et al., 2006; Wang et al., 2003; Andreini et al., 1986; Huang et al., 2005). For olefin metathesis reaction, supported tungsten oxide catalyst is less active than Re and Mo oxide. However, it is attractive for industry because it is tolerant to various poisons in the industrial feed stream (Heckelsb et al., 1968). On a fundamental scale, the activity of tungsten catalyst is influenced by many factors, in which the property of the support is the most important factor due to its influence on the structures and properties of supported tungsten oxide species. Some studies have been devoted to explore the interaction between the support and the dispersed oxide species (Grunert et al., 1989; Hu et al., 2006; Wang et al., 2003; Andreini et al., 1986; Huang et al., 2005). Due to the strong interaction between WO_3 and Al_2O_3, WO_3/Al_2O_3 exhibits low activity for the metathesis (Grunert et al., 1989). However, the activity of WO_3/SiO_2 for metathesis is also mediocre at temperatures lower than 573 K due to the weak interaction between WO_3 and SiO_2 support (Wang et al., 2003). Unlike the catalyst MoO_3/SiO_2–Al_2O_3 (amorphous aluminosilicate) (Aritani et al., 2000), the activity of WO_3/SiO_2–Al_2O_3 is low which is similar to WO_3/SiO_2 for propene metathesis (Xu et al., 1985). Xu et al. (Huang et al., 2007a,b; Liu et al., 2009a,b) reported recently that WO_3/HY–Al_2O_3 exhibited excellent activity for metathesis of ethene and 2-butene at 453 K, due to the decreased interaction between the support and tungsten oxide and the increased Brønsted acidity of the support by adding HY zeolite to γ-Al_2O_3.

It has been documented that the states of WO_3 species in amorphous or crystalline are important to the metathesis activity (Huang et al., 2007a), which depends on the tungsten density and the properties of supports (Thomas et al., 1980; Hua et al., 2011; Harmse et al., 2010). The strong interaction between the alumina and tungsten oxide, which even leads to the formation of aluminum tungstate, could be the reason

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* *Corresponding authors*. Tel.: +86 25 83686115; fax: +86 25 83317761.
E-mail addresses: nianhua@nju.edu.cn (N. Xue), dingwp@nju.edu.cn (W. Ding).
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[1] Present address: School of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an 710054, China.
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that WO_3 supported on alumina shows poor catalytic performance. Coating the γ-Al_2O_3 surface with silica, increasing the acidity of the support and slightly decreasing the interaction between the WO_3 and the support at the same time, would be a good strategy to alter the tungsten state and to increase the activity of 1-butene metathesis.

The present work has demonstrated the dispersion of tungsten species on the supports by combining the characterization results of X-ray diffraction, Raman scattering, UV–vis, H_2-TPR and NH_3-TPD. 1-Butene metathesis was tested and the highest activity was observed on 6 wt.% tungsten loaded γ-Al_2O_3, which was pre-deposited with 20 wt.% silica ($6W/20SiO_2/Al_2O_3$), with 21 mol% propene yield (453 K, 0.1 MPa, WHSV of 2.4 h^{-1}). The suitable dispersion, reducibility of tungsten oxide and acidity of support contributed to the activity.

2. Material and methods

2.1. Synthesis and characterization

Silica modified γ-Al_2O_3: γ-Al_2O_3 (Fu Shun Research Institute of Petroleum and Petrochemicals, 180 $m^2\,g^{-1}$) was immersed into 3-aminopropyl-triethoxylsilane (Aldrich, 99.9%) which was solved in ethanol with constant stirring at room temperature for 2 h. The slurry was dried at 373 K for 12 h and calcined at 823 K for 12 h in air. The silica content was fixed at 10, 20, 30 wt.%. The resulted modified γ-Al_2O_3 supports were designated as $xSiO_2/Al_2O_3$, where x presented the weight mass percentage of SiO_2.

Supported tungsten oxide: The supported tungsten catalysts were prepared by impregnation method. The support was immersed in the solution of ammonia metatungstate at room temperature and stirred for 6 h. The resulted slurry was then dried at 373 K and calcined at 823 K for 8 h in air. γ-Al_2O_3, SiO_2 (Qingdao Haiyang Chemical Co. Ltd., 210 $m^2\,g^{-1}$), SiO_2–Al_2O_3 (Aldrich, 475 $m^2\,g^{-1}$, Al_2O_3 content 13 wt.%) and $xSiO_2/Al_2O_3$ were selected as the supports in the present work. The content of W in every supported catalyst was fixed as 6 wt.%. Tungsten supported on $xSiO_2/Al_2O_3$ was denoted as $6W/xSiO_2/Al_2O_3$, where 6 indicated the loading of W (weight percentage).

X-ray diffraction: XRD patterns of catalysts were recorded in the 2θ region of 20–80° on a *Shimadzu* XRD-6000 with Cu K_α radiation ($\lambda = 1.5418$ Å). The scan speed was set at 10° min^{-1} with a step size of 0.02°.

Surface area: The specific surface areas were measured by means of the nitrogen adsorption at 77 K on a Micrometrics ASAP 2020 instrument. Before N_2 adsorption, the sample was outgassed under vacuum at 573 K for 3 h.

Raman and UV characterization: Raman spectra were recorded with a Renishaw inVia system equipped with a confocal microscope. A 514.5-nm exciting line was focused using a 50× objective lens. UV–vis spectra were recorded with a UV-2401PC spectrometer at room temperature. The spectra were recorded under air-exposed conditions in the range 200–800 nm and the scan speed was 120 nm min^{-1}. $BaSO_4$ powder was used as the reference.

Temperature-programmed desorption and reaction: NH_3-TPD profiles were obtained by using a micromeritics AutoChem TP-5080 apparatus with a thermal conductivity detector. The samples were preteated at 823 K for 2 h in He stream (30 mL min^{-1}) and was then cooled to 373 K. The pretreated sample was exposed to NH_3 stream for 30 min, then purged with a pure He stream for a certain period of time until a constant baseline was obtained. NH_3-TPD was carried out in the range of 373–973 K at a heating rate of 20 K min^{-1}. The acid amount of sample was calculated according to reference. H_2-TPR profiles were obtained by using a micromeritica AutoChem TP-5080 apparatus with a thermal conductivity detector. Under flowing 10% H_2/Ar flow (30 mL min^{-1}), H_2-TPR profiles were obtained in the range of 293–1073 K at a programmed temperature rate of 10 K min^{-1} after the samples had been pretreated in an He flow at 823 K for 2 h.

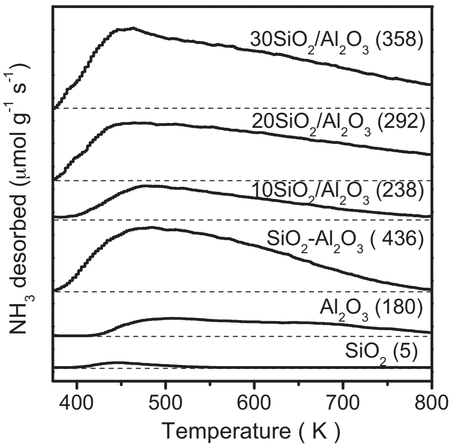

Fig. 1 – NH_3-TPD profiles of all supports in the present work. Values in parentheses represent the density ($\mu mol\,g^{-1}$) of desorbed NH_3 in sample surfaces from 373 to 973 K after steady adsorption.

2.2. Catalytic tests

The 1-butene metathesis reaction was carried out in a continuous-flow, fixed-bed system. A 0.2 g catalyst sample was placed into a quartz wool plug located in a quartz U-tube. After the catalyst was pretreated in situ at 873 K for 2 h under an Argon flow (99.99% purity, 60 mL min^{-1}), it was cooled to the reaction temperature in the Argon flow. Then the Ar was switched to 1-butene (99.5%). The reaction conditions were as following: temperature = 393 K, pressure = 0.1 MPa, WHSV (1-C_4H_8) = 2.4 h^{-1}. The reaction products were analyzed online by gas chromatography with a 50-m fused silica chrompack PLOT Al_2O_3/Na_2SO_4 capillary column and a flame ionization detector.

3. Results and discussion

3.1. The acidity of different supports

In the present work, the NH_3-TPD is used to probe the acidity of supports. Fig. 1 shows the NH_3-TPD results of different supports. Values in parentheses represent the density ($\mu mol\,g^{-1}$) of desorbed NH_3 in sample surface from 373 to 973 K after steady adsorption. A very weak ammonia desorption peak was found at ~450 K on SiO_2, suggesting almost no acidity for this support. The broad desorption peak centering at about 473 K was observed for the other supports. The total amount of the acid sites from NH_3-TPD of the supports decreased in the following sequence: SiO_2–Al_2O_3 > $xSiO_2/Al_2O_3$ > γ-Al_2O_3 > SiO_2. Furthermore, the amount of acid sites in $xSiO_2/Al_2O_3$ increased with increasing the content of silica in γ-Al_2O_3 surface (Fig. 1).