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ScienceDirect
Applied Catalysis A: General 323 (2007) 94–103
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

The effect of calcination time on the activity of WO_3/Al_2O_3/HY catalysts for the metathesis reaction between ethene and 2-butene

Shengjun Huang, Shenglin Liu, Qingjun Zhu, Xiangxue Zhu, Wenjie Xin, Huijuan Liu,
Zaochi Feng, Can Li, Sujuan Xie, Qingxia Wang, Longya Xu *

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

Received 20 August 2006; received in revised form 24 January 2007; accepted 5 February 2007
Available online 13 February 2007

Abstract

A series of WO_3/Al_2O_3/HY catalysts were prepared by thermal spread method (i.e., calcination of physically mixed WO_3, Al_2O_3 and HY zeolite) for the metathesis reaction between ethene and 2-butene to propene. The transformation of tungsten oxide species was studied by the characterization techniques of XRD, H_2-TPR, UV-Vis, UV Resonance Raman, NH_3-TPD and N_2 adsorption–desorption techniques. The thermal spread effect during calcination results in the dispersion of bulk WO_3 phase into microcrystallites on γ-Al_2O_3 surface, followed by a chemical transformation to the monomeric surface tungstate species via the involvement of Brönsted acid sites of HY zeolite. These monomeric surface tungstate species, identified by a characteristic Raman band at 970 cm^{-1}, are crucial for the metathesis activity. We suggest such activity related species are tetrahedrally coordinated. Moreover, it is found that there is an optimal calcination time for the formation of these WO_4^{2-} species and further calcination causes the condensation to the polytungstate clusters, which are less active for the metathesis reaction. The optimized catalyst shows superior catalytic activity of metathesis reaction between ethene and 2-butene to propene at 453 K with 2-butene conversion close to thermodynamic equilibrium value (~64%).

Keywords: Metathesis; Tungsten oxide catalysts; γ-Al_2O_3; HY zeolite; UV-Vis; UV Raman; Surface tungstate

1. Introduction

The olefin metathesis has attracted considerable attention for decades due to its flexibility to produce desired chemical products. Recently, the metathesis reaction between ethene and 2-butene is employed to produce propene owing to the growing needs of propene whereas the demands for ethene and 2-butene are relatively stable. Various transition metal compounds have been tested for the reaction and the most active materials were reported to be rhenium, molybdenum and tungsten species supported on SiO_2 and Al_2O_3 [1–3]. Among those catalysts, WO_3 supported on SiO_2 is of particularly interest to the industry because of its resistance to the impurities, although it has drawbacks of high reaction temperature and relatively low catalytic activity. A successful industrial application of WO_3/SiO_2 for this process is the OCT process licensed to ABB Global [3]. However, the detailed preparation procedures of catalysts and the nature of active sites remain to be moot points.

In addition to the conventional supports of alumina and silica, other types of mixed supports such as SiO_2–Al_2O_3 [4], Al_2O_3–B_2O_3 [5] and Al_2O_3–P_2O_5 [6] were reported for the preparation of catalysts. The advantages of such supports were speculated to be their increase of Brönsted acidity. In contrast to the oxide supports, zeolites are well known for their Brönsted acidity, and we have employed the combination of HY zeolite and γ-Al_2O_3 as mixed supports for WO_3. The resulting catalyst exhibits high activity for the metathesis reaction between ethene and 2-butene at 453 K, which is the lowest reaction temperature among reported tungsten catalysts [7]. Moreover, both the selectivity toward propene and life time of WO_3/Al_2O_3-HY prove to be promising, leading to their potential industrial applications. Typically, supported tungsten oxide catalysts are prepared by impregnation of the support with an aqueous solution of a suitable tungsten precursor compound. After calcination and further treatments, the tungsten species are transformed into the surface tungsten oxide species or

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* Corresponding author. Tel.: +86 411 84379279; fax: +86 411 84693292.
E-mail address: lyxu@dicp.ac.cn (L. Xu).

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doi:10.1016/j.apcata.2007.02.004

crystallites depending on the density of surface tungsten species.

It is extensively reported that the crystalline WO_3 is inactive for the metathesis reaction [8–10] and the dispersed surface tungsten oxide species is believed to be active species precursors. As for the conventional WO_3/SiO_2 and WO_3/Al_2O_3 catalysts prepared by impregnation methods, surface tungsten species are reported to be tetrahedral, octahedral and polytungstate species. Furthermore, it is suggested that the structures of the tungsten species are dependent on the preparation condition, such as tungsten loading, calcination temperature, and the property of the oxide support [11–14], thus the identification of active sites precursors is a challenging task. The most important questions pertaining to the active sites precursors for WO_3/Al_2O_3/HY regard (i) the structure of precursors and (ii) the roles of Al_2O_3 and HY zeolite support in the formation of these species.

In contrast to the impregnation method, another alternative preparation method for active catalysts is thermal spread method with the advantage to avoid handling of impregnation solution. It is reported that crystalline MoO_3 or WO_3 can disperse over the surface of γ-Al_2O_3 with a chemical transformation into a surface molybdate or tungstate by thermal spread method [15–20]. In an attempt to clarify the active species precursors in the metathesis reaction, we carried out systematic studies of a series of WO_3 catalysts prepared by the thermal spread method, which were performed by calcination of mechanical mixture of crystalline WO_3, Al_2O_3 and HY zeolite with different calcination time. The catalytic performances of the metathesis reaction between ethene and 2-butene indicate that the metathesis activity is dependent on the calcination time. The intrinsic influence of calcination time on the evolutions of tungsten species of WO_3/Al_2O_3/HY catalysts was studied by XRD, H_2-TPR, NH_3-TPD, UV-Vis and UV Resonance Raman techniques. A distinct relation between metathesis activity and specific surface tungsten oxide species with characteristic Raman band at 970 cm^{-1} is demonstrated. Furthermore, the function of γ-Al_2O_3 and HY zeolite support for the formation of these active sites are discussed.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of WO_3/Al_2O_3/HY catalysts

γ-Al_2O_3 was obtained from Fushun Catalysts manufactory, China, and was calcined at 773 K for 2 h before use. HY zeolite (Wenzhou zeolite manufactory, $SiO_2/Al_2O_3 \approx 10$, $Na_2O <$ 0.2 wt.%) was also calcined at 773 K for 2 h. The crystalline WO_3 powder was prepared by calcination of ammonium metatungstate at 1073 K for 2 h. The physical mixtures were prepared by first tumbling a portion of the γ-Al_2O_3, HY and WO_3 at weight ratio of 62.2%:26.6%:11.2%. The amount of WO_3 calculated as loading on Al_2O_3/HY support is 12.6 wt.%. These mixtures were hand-ground in an agate mortar for 10 min. After this step, the ground mixtures were calcined at 873 K in simulated air atmosphere for certain time, which was denoted as W(x) and x represents the calcination time in hours.

2.1.2. Preparation of reference sample

A sample of WO_3/Al_2O_3/HY, prepared according to the aforementioned process but without the calcination step, was designated as the reference sample for characterization.

2.1.3. Preparation of WO_3/Al_2O_3 or WO_3/HY

The mixture of Al_2O_3 (or HY zeolite) and the desirable amount of WO_3 were also hand-ground and calcined at 873 K for 18 h, which was denoted as WO_3/HY and WO_3/Al_2O_3, respectively.

2.2. Catalytic evaluation of catalysts

The catalysts were tested in a fixed-bed flow microreactor of 10 mm inner diameter, and 3 g of catalyst with an average particle size of 0.56–1.3 mm was loaded. An EU-2 type thermocouple was fixed in the middle position of the catalyst bed at the outside of steel reactor to measure the temperature of electric furnace, which was taken as reaction temperature. Before catalytic evaluation, the catalyst was pretreated at 773 K for 1 h under high purity N_2 (0.1 MPa, 30 ml min^{-1}). The reactions were performed at 453 K in the atmospheric pressure. The volume concentration of ethene and 2-butene were 30% and 30%, respectively, with the dilute gas of N_2. The employed WHSV was 1.5 h^{-1}. The activity of catalysts was measured by 2-butene conversion, and the metathesis selectivity was defined as the carbon atoms of the desired product of propene divided by the overall carbon atoms in the effluent gas. The possible side reactions were isomerization, secondary metathesis, oligomerization, etc. Since it is difficult to list all the products precisely, the side products are classified by their carbon number as $iC_4^{=}$ & $1{-}C_4^{=}$ and C_5 & C_5^{+}.

2.3. Catalyst characterization

X-ray diffraction (XRD) measurements were performed with an XPert Pro PAnalytical Diffractometer using Cu Kα radiation, operating at 40 kV and 50 mA. Patterns were recorded from 3–70° (2θ).

UV-Vis spectra were recorded with a JASCO 500 spectrophotometer equipped with a diffuse reflectance attachment. The samples were studied in the form of 12-mm-diameter, 2-mm-thick pellets prepared as self-supporting wafers. The spectra were recorded under air-exposed conditions in the range 200–800 nm and the scan speed was 120 nm min^{-1}. The contribution from the Al_2O_3-HY supports has been subtracted from the signal.

The UV Resonance Raman spectra were obtained under ambient condition on a homemade UV resonance Raman spectrograph. A 325.0 nm line from a He–Cd laser was used as the excitation source. The power of the laser lines was below 1.0 mW. Samples were mounted into a spinning holder to avoid thermal damage during the spectrum scanning which usually