

Effect of N₂ Pretreatment on the Properties of Tungsten-Based Catalysts in Metathesis of Ethylene and 2-Butene

K. Aranyarat, S. Maksasithorn, K. Suriye, S. Kunjara Na Ayudhya, J. Panpranot

Abstract—The effect of N₂ pretreatment on the catalytic activity of tungsten-based catalysts was investigated in the metathesis of ethylene and trans-2-butene at 450°C and atmospheric pressure. The presence of tungsten active species was confirmed by UV-Vis and Raman spectroscopy. Compared to the WO₃-based catalysts treated in air, higher amount of WO₄²⁻ tetrahedral species and lower amount of WO₃ crystalline species were observed on the N₂-treated ones. These contribute to the higher conversion of 2-butene and propylene selectivity during 10 h time-on-stream. Moreover, N₂ treatment led to lower amount of coke formation as revealed by TPO of the spent catalysts.

Keywords—Metathesis, Pretreatment, Propylene, Tungsten.

I. INTRODUCTION

OLEFIN metathesis of ethylene and 2-butene is an interesting reaction for propylene production owing to the rising demand of propylene [1]. Propylene production from metathesis of ethylene and 2-butene has been widely investigated using WO₃/SiO₂ catalysts. The performances of supported tungsten oxide catalysts for metathesis reactions were affected by tungsten contents, pretreatment conditions, and the oxidation state of tungsten species [2]-[6].

Typically, prior to reaction the WO₃-based catalysts are pretreated under N₂ flow at an elevated temperature (500-550°C) to get rid of moisture. However, some interaction between tungsten oxide and silica support may occur during the catalyst pretreatment stage and the catalyst activity appeared to depend on conditions of pretreatment due to possible loss of lattice oxygen from tungsten oxide under the above-mentioned conditions of catalyst pretreatment [5]. The catalytic activity was related to the nonstoichiometric state of tungsten oxide.

In the present study, the properties of silica-alumina supported WO₃ catalysts pretreated under N₂ or air at 500°C were investigated in the metathesis of ethylene and 2-butene. The UV-Vis spectroscopy and FT-Raman spectroscopy were

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used to evaluate the amount of tungsten active species which were correlated with the catalyst activity.

II. EXPERIMENTAL

A. Catalyst Preparation

The supported WO₃-based catalysts were prepared using a silica-alumina (Sigma-Aldrich) as the support. The 9 wt% of WO₃ loading was obtained by the incipient wetness impregnation method with an aqueous solution of ammonium metatungstate hydrate (Sigma-Aldrich). The impregnated samples were dried in ambient air for 2 h and subsequently at 110°C overnight in an oven following by calcination in air at the temperature sufficiently removing the residue during the synthesis for 8 h.

B. Catalyst Characterization

1. FT-Raman

The molecular structure of the supported tungsten oxide was determined using Raman spectroscopy. The Raman spectra of the samples were recorded using a PerkinElmer Spectrum GX spectrometer, collected by projecting a continuous wave YAG laser of Nd (810 nm) through the samples at room temperature. A scanning range of 200–1400 cm⁻¹ with a resolution of 2 cm⁻¹ was applied.

2. UV-Vis Spectroscopy

The surface structure of tungsten oxide species was investigated by the Diffuse Reflectance UV-Vis Spectroscopy. The samples were examined on Lambda 650 UV-Vis spectrometer in the range 200-800 nm at ambient temperature.

3. Temperature Programmed Oxidation (TPO)

The amount of carbon deposit was determined from the amount of CO₂ by using the temperature programmed oxidation (TPO) of the spent catalyst. 0.5 g of each catalyst was placed in quartz tube under the 1% O₂/He flow and heated with the heat rate of 5°C/min from room temperature to 900°C. Oxygen consumption and formation of reaction product as CO₂ were monitored by agilent gas chromatograph (7820A) equipped with TCD.

C. Catalytic Performance Testing

The catalysts were tested in the gas-phase metathesis reaction by using 2% trans-2-butene with excess ethylene in nitrogen as the reactant feed. A fixed-bed reactor (ID tube =

19.05 mm) under atmospheric pressure with 3 g of the catalyst was used for the reaction. The weight hourly space velocity (WHSV) was 0.36 h^{-1} . In a typical test, the catalyst was pretreated at 500°C in N_2 or Air and then cooled down to reaction temperature at 450°C under the same gas. The samples were taken every 30 min interval during the 10 h time-on-stream. The reaction products were analyzed on line by GC analysis with an Agilent 7820A gas chromatograph equipped with a GS-Gaspro 113-4362 capillary column.

III. RESULT AND DISCUSSION

The UV-Vis spectra of the WO_3 -base catalysts pretreated under N_2 and air are shown in Fig. 1. According [7], the absorption band at 236 nm corresponds to isolated WO_4^{2-} tetrahedral species and the adsorption band at 280 nm can be assigned to octahedral polytungstate species. Whereas the third band at around 400 nm corresponds to WO_3 crystalline species. In this work, the results clearly show that pretreatment under different atmospheres affected the formation of active tungsten species. The N_2 -treated catalysts exhibited higher intensity of the isolated species (at 236 nm) than the air-treated catalysts.

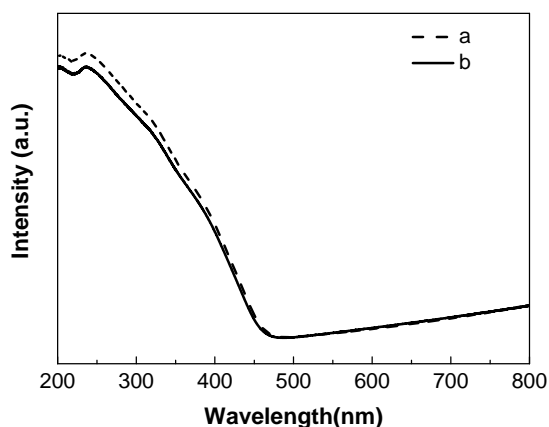


Fig. 1 UV-Vis spectra of WO_3 -based catalysts pretreated under N_2 (a) and air (b)

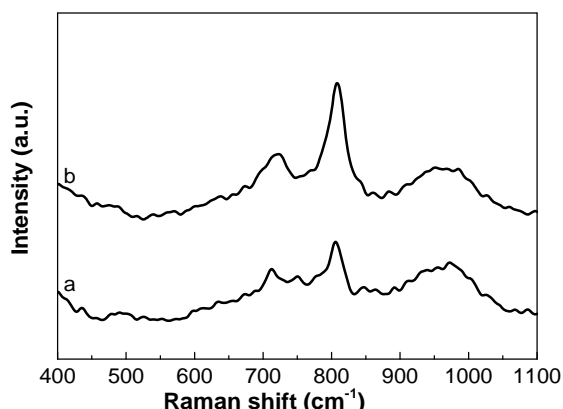


Fig. 2 FT-Raman spectra of WO_3 -based catalysts pretreated under N_2 (a) and air (b)

To determine the tungsten species presented on the supported catalysts, the FT-Raman spectra was used and the results are shown in Fig. 2. The Raman bands at 498, 602, 808 and 1060 cm^{-1} were assigned to the characteristic vibration of four- and three-member silica rings and Si-O-Si stretching, respectively [8]. The bands at 263–275, 707–720, and $807\text{--}808 \text{ cm}^{-1}$ were assigned to the deformation mode of W–O–W, bending mode of W–O, and symmetric stretching mode of W–O, respectively [9]. The broad band at 970 cm^{-1} was assigned to the O=W=O band of isolated surface tetrahedral tungsten oxide species [9], which was reported as the active species formetathesis [10]. Interestingly, the N_2 -treated catalysts had higher intensity of isolated species (at 970 cm^{-1}) and lower intensity of crystalline species (at 807 cm^{-1}) than the air-treated ones. Such results suggest a better tungsten dispersion on the catalysts. The FT-Raman results were consistent with the UV-Vis results. It is confirmed that pretreatment under N_2 resulted in higher amount of active tungsten species being formed.

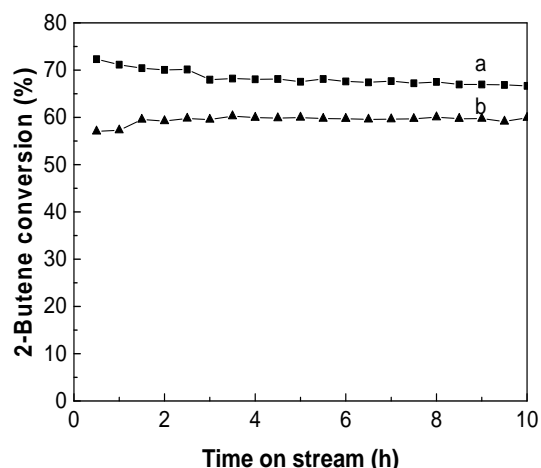


Fig. 3 2-Butene conversion over N_2 -treated catalysts (a) and air-treated catalysts (b)

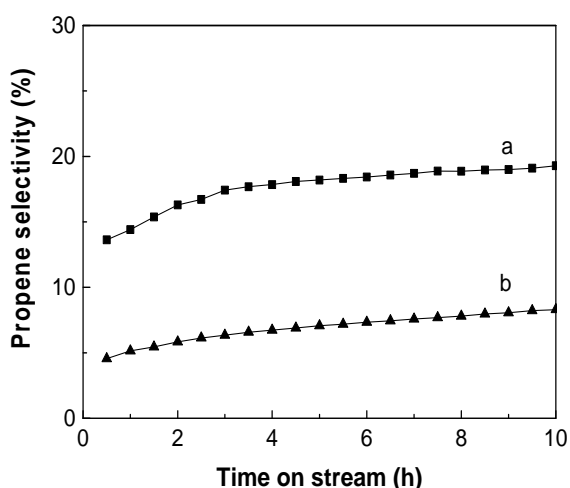


Fig. 4 Propylene selectivity over N_2 -treated catalysts (a) and air-treated catalysts (b)

The metathesis activity of WO_3 -based catalysts pretreated under N_2 and air was investigated at 450°C and atmospheric pressure. The results are shown in Figs. 3 and 4. The conversion of 2-butene (Fig. 3) of the N_2 -treated catalysts was about 66% whereas pretreatment under air showed 60% conversion of 2-butene. The propylene selectivity is another considerable parameter related to the performance of catalysts. The propylene selectivity (Fig. 4) of the N_2 -treated catalyst was 19% whereas the air-treated catalysts exhibited 8% of propylene selectivity. Side products such as cis-2-butene and 1-butene could occur via isomerization as can be seen in Fig. 5. The selectivity of these by-products was lower on the N_2 -treated catalyst. The metathesis activity is dependent on amount of active sites of tungsten which is WO_4^{2-} tetrahedral species [7]. In addition, an increase in the amount of WO_3 crystalline species which is not an active site for metathesis reaction, resulting in the reduction of metathesis activity [11]. According to the FT-Raman and the UV-Vis results, it is suggested that higher amount of WO_4^{2-} tetrahedral species and lower amount of WO_3 crystalline species were formed on the N_2 -treated catalysts, resulting in higher activity than the air-treated ones. Nevertheless, both N_2 - and air-treated catalysts showed good catalytic stability during the 10 h time-on-stream.

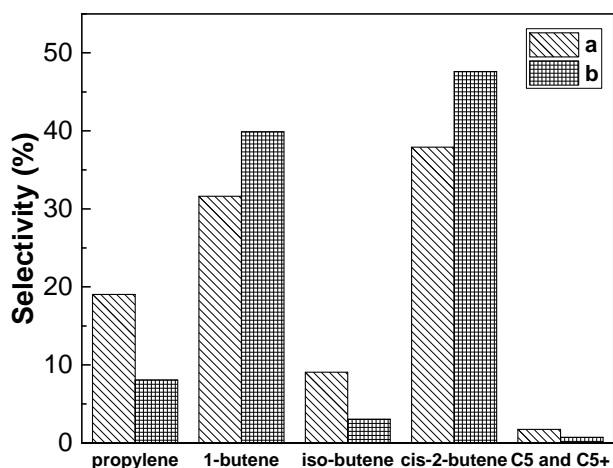


Fig. 5 Products distribution over N_2 -treated catalysts (a) and air-treated catalysts (b)

The O_2 -TPO was used to characterize the coke species on catalysts after 10 h of the reaction. As shown in Fig. 6, the catalysts displayed 2 peaks of coke burning. Peak positions in TPO profiles of the catalysts are related to the coke species at different locations. The oxidation peak at 470°C is mainly from hydrocarbons associated with metal species. The temperature oxidation peak at 630°C is assigned to carbonaceous deposits on strong acid sites, mostly Brønsted acid sites in the silica-alumina support. The total amount of carbon formation per gram of catalysts was shown in Fig. 7. It was found that the N_2 -treated catalysts showed lower amount of coke deposit than the air-treated ones. This finding may be

beneficial for its further application in industry.

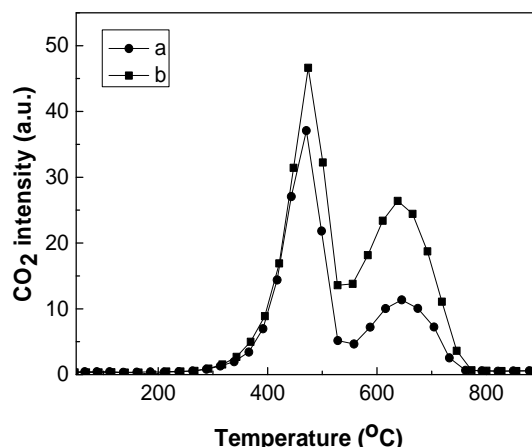


Fig. 6 TPO profiles of WO_3 -based catalysts pretreated under N_2 (a) and air (b)

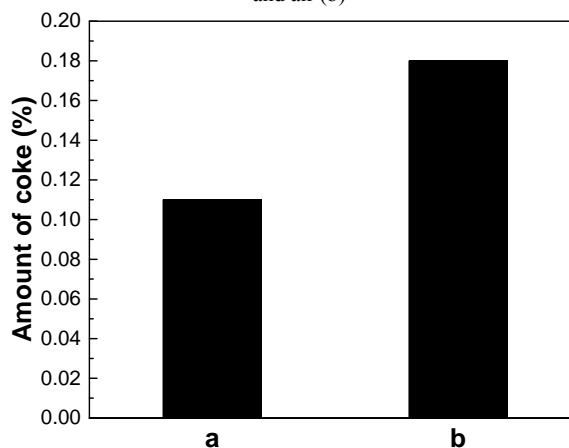


Fig. 7 Amount of coke per gram of WO_3 -based catalysts pretreated under N_2 (a) and air (b)

IV. CONCLUSION

This work aims to study the effect of different atmospheric pretreatments (N_2 and air) on the catalytic activity of WO_3 -based catalysts in the metathesis reaction of ethylene and 2-butene for propylene production. The N_2 -treated catalysts exhibited higher activity and propylene selectivity than the air-treated ones. The improved catalyst performances were correlated well to the higher amount of WO_4^{2-} tetrahedral species and lower amount of WO_3 crystalline species as revealed by FT-Raman and UV-vis results. The N_2 treated catalysts also showed lower amount of coke deposit after the 10 h time-on-stream. Thus, N_2 -pretreatment is a good strategy to enhance the catalyst performances with good stability.

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