

The Structure-reactivity Relationship for Metathesis Reaction between Ethylene and 2-butene of WO₃/SiO₂ Catalysts Influenced by Different Calcination Temperature

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Abstract. The effect of calcination temperatures on the active species of WO₃/SiO₂ catalysts for propylene production from metathesis of ethylene and 2-butene was studied to elucidate the structure-reactivity relationship. The influence of calcination temperatures on catalyst physicochemical properties, relating to the active species, was summarized from an array of characterization results. It has been found that the surface tetrahedral tungsten species with high metal support interaction were formed on the catalyst calcined at 550 °C as confirmed by Raman, UV-Vis and H₂-TPR spectra, respectively.

Keywords: Metathesis; Silica-support tungsten; Structure-reactivity

1. Introduction

One of the processes used for the production of propylene is the metathesis reaction between ethylene and 2-butene in the presence of a suitable catalyst. Several researchers have reported tetrahedral tungsten oxide species as the active sites for metathesis reaction of ethylene and 2-butene [1, 2]. Huang et al. [3–5] found that Brønsted acidity promotes the formation of active species for metathesis. Liu et al. [6] reported that the moist air accelerates the transformation of bulk WO₃ to surface oxide and reduces the calcination time needed for the preparation of a highly active catalyst. Spamer et al. [7] found that the active tungsten surface compound is involved in the interaction with the support. Roosmalen et al. [2] suggested that the acidity needed for the formation of the initial metal carbene is available from a Lewis site-alkene complex located on the transition metal ion. Nevertheless, the effect of calcination temperatures on the metathesis activity has not been extensively investigated and the structure-reactivity relationship of the silica supported tungsten catalyst has not been reported earlier. Therefore, this study has been focused on the influence of calcination temperatures on the nature of tungsten species of WO₃/SiO₂ that are active in the formation of propylene and by-products by the metathesis reaction of ethylene and 2-butene.

2. Experimental

Silica gel, Davisil grade 646 (pore volume: 1.15 cm³/g, supplied by Aldrich) was used as support. The precursor of 8% WO₃/SiO₂ was prepared by impregnation of the silica with an aqueous solution of ammonium metatungstate hydrate (Aldrich, 99.9%). The sample was dried at 110 °C for 12 h. and calcinated temperatures were denoted as W(450), W(550), W(650) and W(750) respectively.

3. Results

Catalyst Characterization: The XRD patterns of W(X) catalysts are shown in Fig. 1. All W(X) catalysts exhibited the characteristic peaks of WO₃ crystallite at 2θ of 23.12°, 23.60° and 24.38°. It has been found that the XRD peaks tend to increase in their intensities at higher calcination temperatures. This reflects that various tungsten oxide species other than tungsten crystal (WO₃) occurred during the course of calcinations. As shown in Table 1, the BET surface area of the catalyst decreased with the higher calcination temperatures. This may probably due to either the sintering among tungsten metal itself and/or tungsten metal and silica support.

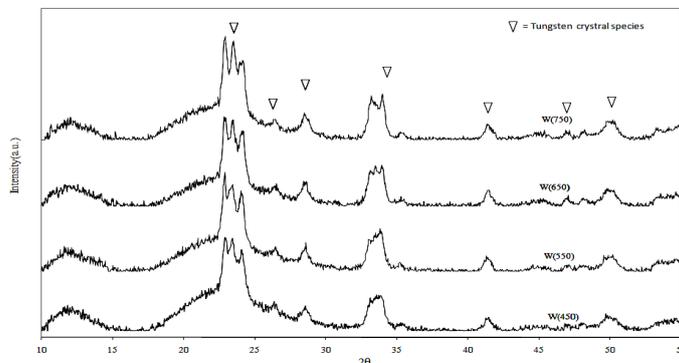


Fig. 1: X-ray diffraction pattern of the silica-supported tungsten catalysts calcined at different temperatures.

Table 1: Specific surface area of WO₃/SiO₂ catalysts at difference temperature calcinations

Sample	Pure SiO ₂	W(450)	W(550)	W(650)	W(750)
surface area/ m ² ·g ⁻¹	256.9	234.1	238.9	222.2	173.9

As for the catalyst acidity determination (NH₃-TPD) shown in Fig.2, the low temperature peak around 200 °C corresponding to the weak acid site decreased by amount 75 % at the calcination temperature of 750 °C compared with that of 450 °C. In accordance with the lowered BET surface area, the decrease of acidity was also affected by the higher calcination temperatures.

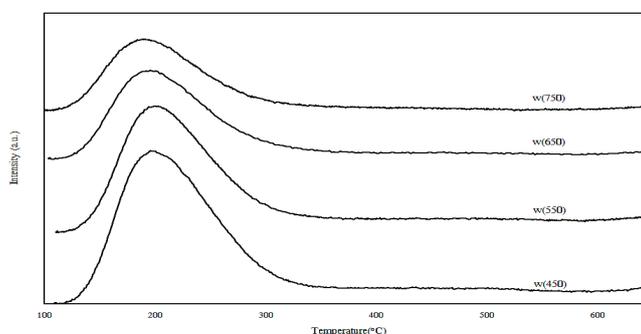


Fig. 2: NH₃-TPD profiles for W(X) catalysts calcined at different temperatures.

Raman spectroscopy was adopted as a good tool for determination of the structure of tungsten species in supported WO₃/SiO₂ catalysts calcined at different temperatures, W(X). As shown in Fig.3, the Raman band characteristics at 498, 602, 808, 1060 cm⁻¹ were assigned to vibration of four-and three-membered silica ring and Si-O-Si stretching[8]. The positions of the Raman band for crystalline WO₃ at 263-275, 707-720 and 805-808 cm⁻¹ were assigned to the deformation mode of W-O-W, bending mode of W-O, respectively. The band at 970 cm⁻¹ was assigned to the surface tungsten oxide species, the active species for metathesis reaction [9], as reported by the O=W=O band of the isolated surface tetrahedral tungsten oxide species[10]. The bands around 710, 808, 970 cm⁻¹ differed in intensity were observed (Fig 3). Since the tungsten content for all the catalysts is the same, we suggested that the amount of surface tungsten oxide compound can be estimated from the relative intensities(*I*) of Raman bands between 970 and 805 cm⁻¹ as adopted by some researchers [4,11] It has been found that the maximum ratio of *I*₉₇₀/*I*₈₀₅ was achieved for the catalyst calcined at 550 °C. The relative reducibility of oxygen on catalyst surface by hydrogen, the H₂-TPR technique was used to investigate the interaction between tungsten species and silica support as shown in Fig.4. It has been

found that the calcination temperature influenced both the position and area of reduction peaks of each W(X) catalyst. The catalyst calcined at 550 °C, W(550), exhibited the shift of H₂-TPR peaks at relatively higher temperature and show remarkably less consumption of H₂ compared to the other samples. This indicates the existence of the high metal-support interaction for W(550) catalyst and reflects the influence of calcination temperature towards the tungsten species obtained. The catalyst calcined at 550 °C, W(550), was found to possess high metal-support interaction as clearly indicated by H₂-TPR result in Fig.4. Moreover, the substantial existence of surface tetrahedral tungsten oxide species was also noticeable by Raman result in Fig.3. Therefore, this reveals some interesting relationship between the tetrahedral species and high metal-support interaction.

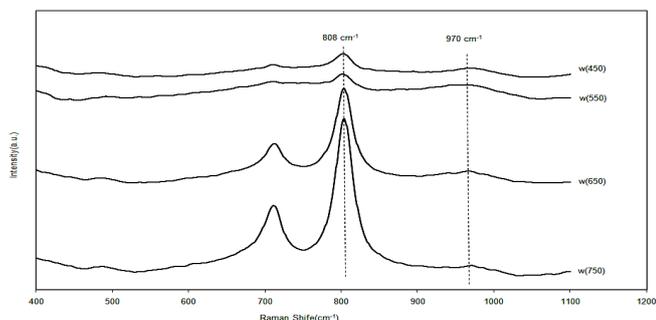


Fig. 3: Raman spectra samples W(X) catalysts calcined at different temperatures.

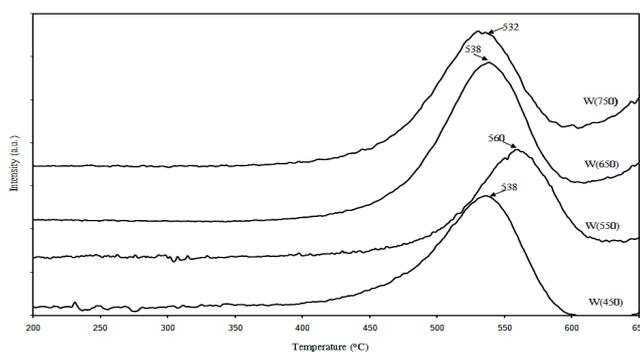


Fig. 4: H₂-TPR profile W(X) catalysts with different calcination temperatures.

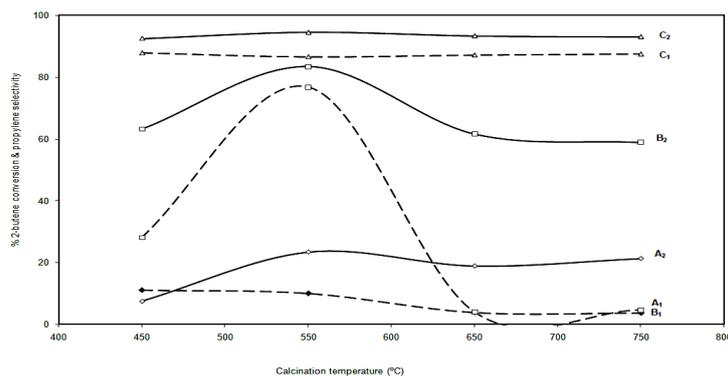


Fig. 5: Metathesis activity on tungsten catalysts calcined at different temperatures for 8 h on stream; A, B and C denote reaction temperatures of 300, 400 and 500 °C, respectively; 1 and 2 denote 2-butene conversion and propylene selectivity, respectively.

The trans-2-butene conversion and propylene selectivity of various catalysts calcined at different reaction temperatures are shown in Fig 5. As high as 85.6% of trans-2-butene conversion and 80.6% of propylene selectivity were obtained on W(550) at 400 °C. It is interesting to note that both trans-2-butene conversion and propylene selectivity markedly decreased for catalyst calcined at temperatures lower or

higher than 550 °C, in spite of the same reaction temperature at 400 °C. At reaction temperature of 300 °C, the considerably low trans-2-butene conversion and propylene selectivity were observed almost irrespective of calcination temperatures. As for the reaction of 500 °C, the relatively high trans-2-butene conversion and propylene selectivity were kept almost constant, regardless of the calcination temperatures as well.

4. Discussion

The results obtained have shown the influence of calcination temperatures on the catalyst activity. The structure-reactivity relationship of WO₃/SiO₂ catalysts was conceived from an array of characterization results such as metal-support interaction, acidity, surface tungsten species, for example. It has been widely proposed that the surface tetrahedral tungsten oxide species are the active site for the formation of metathesis products. The catalyst sample of W(550) calcined at 550 °C, exhibiting the highest yield of propylene in this study, possessed the surface tetrahedral tungsten species as confirmed by Raman peak at 970 cm⁻¹ shown in Fig.3. High dispersity of tetrahedral tungsten species on the support is also a prerequisite for the formation of sufficiently active and stable W carbene species. Most likely, the pretreatment of the catalyst at 550 °C results in a high dispersion of the tetrahedral species required for the propene extrusion via metathesis. Moreover, W(550) catalyst showed the high metal-support interaction as indicated by the shift to higher temperature of H₂-TPR shown in Fig.4. Thus, the active site for propylene formation from metathesis should be the surface tetrahedral tungsten oxide species with the high metal-support interaction.

It has been reported elsewhere [9] that brönsted acid sites favored the formation of propylene from metathesis reaction; however, less acidity was obtained at higher calcination temperature in this study. As the brönsted acidity decreased and Lewis acidity increased at higher temperature, the high propylene yield obtained on the catalyst calcined at 550 °C seems to be not influenced by the decrease in brönsted acidity. On the other hand, the increased formation of by-products of 1-butene and cis-2-butene obtained on the catalyst calcined at temperatures higher than 550 °C was accompanied with the increase in Lewis acidity. Thus, the Lewis acidity may, among the other parameters, contribute to the formation of such by-products. The possible formation of crystallites or polytungstate at higher calcination temperatures than 550 °C may be responsible for the formation sites of the side reaction products of 1-butene and cis-2-butene favored by the presence of Lewis acidity.

The existence of surface tetrahedral tungsten species for W(550) catalyst markedly promotes both 2-butene conversion and propylene selectivity in metathesis reaction particularly at 400 °C as clearly seen in Fig.5. However, such influence was less dominated for the reaction at 300 °C, and almost no significant effect of calcination temperature was observed for the reaction at 500 °C. It is believed that the metallocarbene effect also plays an important role for metathesis activity in addition to the availability of surface tetrahedral tungsten species. The reaction temperature of 300 °C may be too low for the exertion of metallocarbene effect, and thus the relatively low conversion and selectivity was observed for all the catalyst samples irrespective of the calcination temperature. On the other hand, the reaction temperature of 500 °C should be high enough for the activation of the metallocarbene effect, and therefore the considerably high metathesis activity was noticed for all the catalyst samples regardless of the effect of calcination temperature. It is also interesting to note that the formation of 1-butene and cis-2-butene was inversely related to that of propylene, while the formation of 1,3-butadiene was almost independent to that of propylene. Thus, it is conceivable that the site for 1-butene and cis-2-butene formation may be another site other than the tetrahedral tungsten active site for propylene formation. The possible formation of crystallites or polytungstate at higher calcination temperatures than 550°C may be responsible for the formation sites of such side reaction products. The site for 1,3-butadiene formation, however, should be different from those for propylene and side reaction products of 1-butene and cis-2-butene formation which is the subject of further investigation.

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