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Propylene Self-Metathesis to Ethylene and Butene over WO_x/SiO_2, Effect of Nano-Sized Extra Supports (SiO_2 and TiO_2)

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Abstract**—**Propylene self-metathesis to ethylene and butene was studied over WO_x/SiO_2 catalysts at 450°C and atmospheric pressure. The WO_x/SiO_2 catalysts were prepared by incipient wetness impregnation of ammonium metatungstate aqueous solution. It was found that, adding nano-sized extra supports (SiO_2 and TiO_2) by physical mixing with the WO_x/SiO_2 enhanced propylene conversion. The UV-Vis and FT-Raman results revealed that WO_x could migrate from the original silica support to the extra support, leading to a better dispersion of WO_x. The ICP-OES results also indicate that WO_x existed on the extra support. Coke formation was investigated on the catalysts after 10 h time-on-stream by TPO. However, adding nano-sized extra supports led to higher coke formation which may be related to acidity as characterized by NH_3-TPD.

Keywords**—**Extra support, nanomaterial, propylene self-metathesis, tungsten oxide.

I. INTRODUCTION

At present, metathesis of ethylene and 2-butene to propylene (1) is interesting due to increasing of propylene demand. In the future, other light olefins may be more demanded. Its reverse reaction, propylene self-metathesis to ethylene and 2-butene (2), can play an important role in petrochemical industry as well [1].

$$CH_2{=}CH_2 + CH_3CH_2{=}CH_2CH_3 \rightarrow 2CH_3CH_2{=}CH_2 \qquad (1)$$

$$2CH_3CH_2{=}CH_2 \rightarrow CH_2{=}CH_2 + CH_3CH_2{=}CH_2CH_3 \qquad (2)$$

One of the common heterogeneous catalysts used in olefin metathesis is WO_3/SiO_2 catalyst due to high poison resistance and long life time [2]. Improvement of metal oxide dispersion is one of choice to reach high catalytic activity. There are many investigations on dispersion of active species [2]-[7]. Zhao et al. mentioned that dispersion of surface tungsten species is important for the active site formation [3]. In the previous work from our group, [4] reported that high dispersion of tungsten oxide on mixed SiO_2–TiO_2 support enhanced *trans*-2-butene conversion and propylene selectivity. The catalyst development by adding extra support could simply apply to industry without modifying on the main catalysts. Limsangkass et al. [8] reported that adding nano-sized SiO_2 support enhanced conversion, products yield, and induction period than micro ones. They found that tungsten could migrate from the original support to the nano-sized SiO_2 support during thermal treatment, leading to better tungsten dispersion. This phenomenon is called "thermal spreading". It was mentioned that the driving force for thermal spreading is the difference of surface energy of the two metal oxides [9]-[11]. In this work, the type of nano-sized extra supports was investigated on the catalytic performance and coke formation over WO_x/SiO_2 catalysts in the self-metathesis of propylene.

II. EXPERIMENTAL

A. Catalyst Preparation

The catalysts were synthesized by the incipient wetness impregnation method to achieve the nominal loadings of W 9 wt. %. The impregnation was conducted in a flask containing 3 g of silica gel (Davisil grade 646 supplied by Aldrich) with 4.5 cm^3 of an aqueous solution containing the required amount of ammonium metatungstate hydrate (Aldrich, 99.9%). The flask was shaken continuously during impregnation to ensure homogenous distribution of metal on the support. After impregnation, the impregnated sample was dried in ambient air for 2 h and subsequently in an oven at 110°C overnight, following by calcination at more than 500°C in air flow. Finally, the WO_x/SiO_2 was obtained. Nano SiO_2 was supplied by Aldrich and TiO_2 (P25) was supplied by Degussa. The WO_x/SiO_2 and extra supports (SiO_2, TiO_2 and inert ball) were physically mixed in a flask by the ratio 7:3. The flask was shaken for a moment to obtain the homogenous mixture. Finally, WO_x/SiO_2 + TiO_2, WO_x/SiO_2 + SiO_2, and WO_x/SiO_2 + inert ball were obtained.

B. Catalyst Characterization

BET surface area was performed with nitrogen as adsorbate at -196°C after pre-treatment of the samples at 200°C under nitrogen flow. For examination of the single point surface area, the samples were examined from nitrogen adsorption by using Micrometrics Chemisorbs 2750.

The samples containing metallic particulates were digested by hydrochloric acid, hydrofluoric acid and nitric acid, then analyzed to analyze wt. % of metal in the samples by inductively coupled plasma optical emission spectroscopy (ICP-OES).

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The surface structure of tungsten oxide species was investigated by the Diffuse Reflectance UV–Vis Spectroscopy. The sample was examined on Lambda 650 UV–Vis spectrometer in the range 200-800 nm at ambient temperature. The Diffuse reflectance UV–Vis spectrum was deconvoluted by Fityk program to analyze the structure of tungsten oxide species on the surface of the supports.

The surface structure of tungsten oxide species was carried out by FT-Raman spectroscopy from NXR FT-Raman model Fof spectrometer. The samples were performed at ambient temperature with 50 mW power of laser with a scanning range of 300-1200 cm^{-1} and a resolution of 16 cm^{-1}. The samples were collected by projecting a continuous wave YAG laser of Nd (810 nm) with 100 mW power through the samples at room temperature with the scanning range of 200-2000 cm^{-1} and resolution of 16 cm^{-1}.

Total acid of catalysts was measured by temperature program desorption of NH_3 (NH_3-TPD), using a Micromeritic Chemisorb 2750 automated system. The sample was pretreated in a He flow at the temperature not greater than 600°C for 1 h and cooled down to room temperature before 15%NH_3/He mixed gas was flowed over the sample for 1 h to adsorb on the acid sites. Then the excess ammonia was eradicated by the He flowing at the room temperature for 2 h. The catalyst was heated and the TPD profile was detected by TCD detector and analyzed with a ChemiSoft TPx software.

The amount of coke was examined by the temperature programmed oxidation (TPO). The spent catalyst was placed in the reactor under the 1%O_2/He flow and heated with the heat rate of 5°C/min until the temperature reached 700°C, analyzed by GC-8AIT.

C. Catalytic Performance Testing

3 g of catalyst sample was placed at the center of stainless steel tubular reactor with inner diameter (ID) of 7.5 mm and mounted with a type K thermocouple. The catalyst was pretreated at 500˚C under nitrogen flow for 1 h and cooled down to reaction temperature at 450˚C. Catalytic activity for propylene self-metathesis was measured at atmospheric pressure, 450˚C, 20 cm^3/min of 9% propylene in nitrogen, for 10 h time-on-stream. The composition of the feed flow and of the reaction products was analyzed through gas chromatography by using Agilent 7820A gas chromatograph equipped with a column of packed HP-PLOT Al_2O_3 “M” deactivated (50 m with 8 μm ID) and a flame ionization detector using nitrogen as the carrier gas (5 cm^3/min).

III. RESULTS AND DISCUSSION

The dispersion of WO_x on the support was improved to obtain high catalytic activity by thermal spreading concept. The nano SiO_2 and TiO_2 supports with the different surface energies (see Table I) [12], [13] were mixed with the WO_x/SiO_2. Inert ball was also mixed the WO_x/SiO_2 and used as the reference catalyst. After thermal treatment, the nano-sized SiO_2 and TiO_2 were separated from the WO_x/SiO_2 catalysts by sieving and the separated extra supports were analyzed to find the amount of tungsten by ICP-OES. The results show that tungsten was found on the separated TiO_2 more than on the SiO_2 but it was not found on the inert ball. The amount of tungsten on the extra support was related to the surface energy as shown in Table I. The high surface energy representing greater level of instability as the driving force for attracting tungsten from the main support to itself, leading to high tungsten dispersion over the main support [9], [14].

TABLE I
SURFACE ENERGY OF NANO-SIZED EXTRA SUPPORTS

Catalysts	Surface energy (J/m^2)	Concentration of tungsten on the extra support (%)
SiO_2	0.1	2.80
TiO_2	0.9	3.85

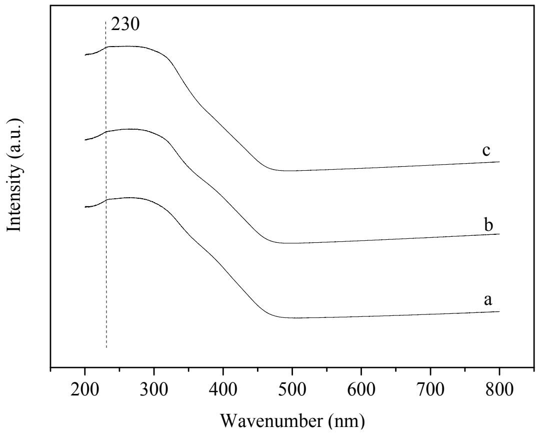

Fig. 1 UV-vis spectra of WO_x/SiO_2 catalysts separated from extra support; (a) WO_x/SiO_2 separated from inert ball, (b) WO_x/SiO_2 separated from SiO_2, (c) WO_x/SiO_2 separated from TiO_2

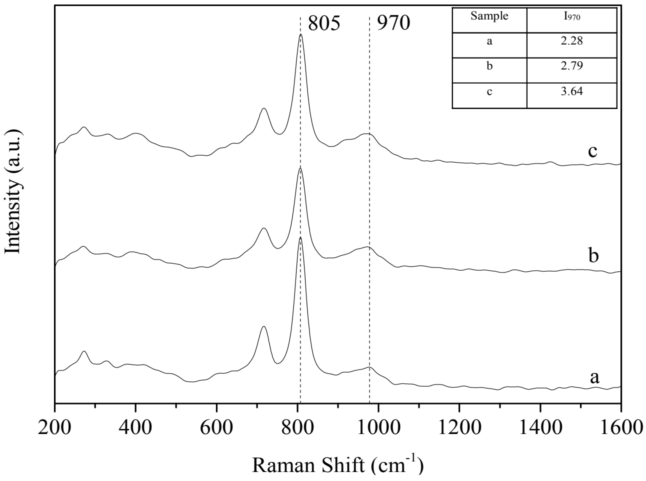

Fig. 2 FT-Raman spectra of WO_x/SiO_2 catalysts separated from extra support; (a) WO_x/SiO_2 separated from inert ball, (b) WO_x/SiO_2 separated from SiO_2, (c) WO_x/SiO_2 separated from TiO_2

The surface structure of the WO_x/SiO_2 after separated from the extra support was examined by UV-vis spectroscopy and the results are shown in Fig. 1. The peak at about 230 and 310 nm were ascribed to W^{6+} (isolated WO_4^{2-} tetrahedral species) and W^{6+} (distorted tetrahedral WO_4^{2-} or octahedral polytungstate species) respectively [3]. From this result, the intensity of band at 230 nm of separated WO_x/SiO_2 from TiO_2 was higher than the other extra supports, indicating that more active site precursors were found over the $WO_x/SiO_2 + TiO_2$. In addition, the FT-Raman spectroscopy results were considered. The Raman bands of surface tungsten oxide species were found on the separated WO_x/SiO_2 from extra support as shown in Fig. 2. The Raman band of 970 cm^{-1} was assigned to be the O=W=O bond of the tetrahedral tungsten oxide species which is considered to be an active site precursor of metathesis reaction. The Raman band of 805 cm^{-1} was assigned to be the stretching mode of W–O–W (crystalline WO_3), which is not the active site precursors [4], [15]. From Fig. 2, the intensity of 970 cm^{-1} for separated WO_x/SiO_2 from the extra support were: WO_x/SiO_2 + TiO2 > $WO_x/SiO_2 + SiO_2$ > WO_x/SiO_2 + inert ball. It is indicated that adding nano-sized extra support improved the dispersion of WO_x on SiO_2 (original support). However, decreasing of the intensity of 805 cm^{-1} in nano-sized extra support system indicated that the migrated tungsten oxide into extra support might be in the form of crystalline WO_3.

The catalytic activities of WO_x/SiO_2 + extra support are shown in Fig. 3. It is well known that improvement of tungsten oxide species dispersion enhances the activity [4], [5]. Propylene conversion of the catalysts mixed with nano-sized extra support was obviously improved, in the following order: $WO_x/SiO_2 + TiO_2$ (6.9%) ~ $WO_x/SiO_2 + SiO_2$ (7.3%) > WO_x/SiO_2 + inert ball (3.6%). However, $WO_x/SiO_2 + TiO_2$ catalyst clearly exhibited the shorter induction period than $WO_x/SiO_2 + SiO_2$ due to higher WO_x dispersion and suitable of WO_x species for yielding the metal carbine species as revealed by the ICP-OES, UV-vis and FT-Raman results [1]. It is concluded that higher surface energy of nano-sized extra support is the driving force for thermal spreading, leading to higher dispersion of WO_x on the original support. The product selectivity is shown in Fig. 4. Adding the nano-sized extra support slightly decreased the main product selectivity (ethylene and butene) with the formation of C_5+ products.

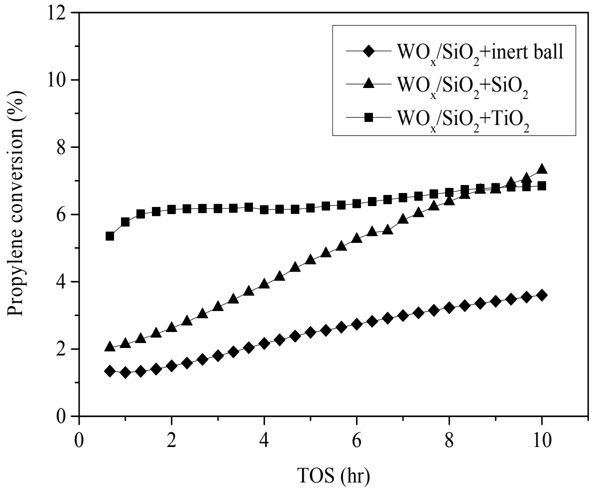

Fig. 3 Propylene conversion for 10 h time-on-stream

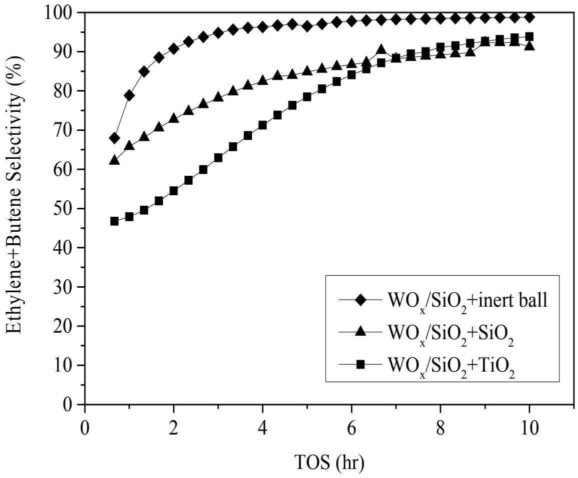

Fig. 4 Ethylene+Butene products selectivity for 10 h time-on-stream

TABLE II
SURFACE AREA, ACIDITY AND COKING OF CATALYSTS

Catalysts	S_{BET} (m^2/g)	Acidity (μmol NH_3/g.cat)	Amount of coke (%)
WO_x/SiO_2 + inert ball	95.3	77.4	0.07
$WO_x/SiO_2 + SiO_2$	147.8	136.0	0.15
$WO_x/SiO_2 + TiO_2$	111.0	145.5	2.68

The BET surface area, total acidity, and the amount of coke of the catalysts are shown in Table II. The acidity was obtained from integrating the area of the NH_3-TPD profile as shown in Fig. 5. Adding nano-sized extra support led to higher acidity and higher amount of coke on the catalysts compared to adding inert ball. It is generally known that coke is catalyzed by acid site through coke precursor which is olefins or aromatic. Then coke precursor was polymerized to form high molecular weight polynuclear aromatic and condensed as coke [16], [17].

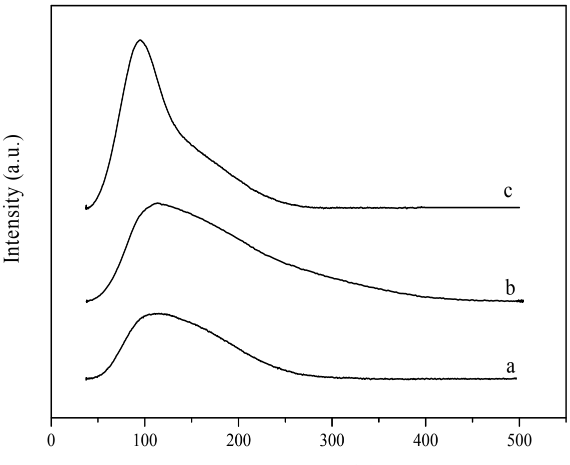

Fig. 5 NH_3-TPD profile of WO_x/SiO_2 catalysts mixed with the extra supports; (a) WO_x/SiO_2 + inert ball, (b) $WO_x/SiO_2 + TiO_2$, (c) $WO_x/SiO_2 + SiO_2$

IV. CONCLUSION

Adding nano-sized extra supports (SiO_2 and TiO_2) improved dispersion of tungsten oxide via thermal spreading. Surface energy of extra support is the driving force for thermal spreading, leading to migration of tungsten oxide from original support to an extra support corresponding to the ICP-OES, UV-vis and FT-Raman results. The better dispersion of tungsten oxide on the catalysts mixed with nano-sized extra support enhanced propylene conversion and clearly exhibited the shorter induction period. Coke formation was correlated to the acid sites on the catalysts.

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