

# Influence of MgO Physically Mixed with Tungsten Oxide Supported Silica Catalyst on Coke Formation

T. Thitiapichart, P. Prasertdama

**Abstract**—The effect of additional magnesium oxide (MgO) was investigated by using the tungsten oxide supported on silica catalyst ( $\text{WO}_x/\text{SiO}_2$ ) physically mixed with MgO in a weight ratio 1:1. The both fresh and spent catalysts were characterized by FT-Raman spectrometer, UV-Vis spectrometer, X-Ray diffraction (XRD) and temperature programmed oxidation (TPO). The results indicated that the additional MgO could enhance the conversion of trans-2-butene due to isomerization reaction. However, adding MgO would increase the amount of coke deposit on the  $\text{WO}_x/\text{SiO}_2$  catalyst. The TPO profile presented two peaks when the  $\text{WO}_x/\text{SiO}_2$  catalyst was physically mixed with MgO. The further peak was suggested that came from coke precursor could be produced by isomerization reaction of undesired product. Then, the occurred coke precursor could deposit and form coke on the acid catalyst.

**Keywords**—Coke formation, metathesis, magnesium oxide, physically mix.

## I. INTRODUCTION

IN the production of propylene, olefin metathesis reaction, which is one of the most reaction, is widely used [1], [2]. The tungsten oxide supported on silica catalyst is commonly applied for this reaction because it can work with the high impurity in feedstock and has a long lifetime [1], [3]-[5]. The amount of tungsten loading was investigated in many studies and found that the optimal amount of tungsten loading on metathesis activity of 2-butene and ethylene is about 8-12 %wt [3], [6]. Many researches have studied and developed on metathesis catalytic activity and deactivation by coke formation [5], [7]-[13]. The basic metal oxide such as magnesium oxide and calcium oxide may be physically admixed with the metathesis catalyst to enhance the reaction [2], [14]. In this study, the effect of additional MgO physically mixed with  $\text{WO}_x/\text{SiO}_2$  catalyst in a weight ratio of 1:1 on catalytic performance and coke deposition was investigated in olefins metathesis reaction of ethylene and trans-2-butene.

## II. EXPERIMENTAL DETAILS

### A. Catalyst Preparation

The main catalyst  $\text{WO}_x/\text{SiO}_2$  was prepared by incipient wetness impregnation method [6], [11]-[13], [15], [16]. The

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ammonium metatungstate hydrate solution was added to the silica gel (35-60 mesh) support and leaved at room temperature for 2 hours. Then, the catalyst was dried at 110°C in an oven and calcined at temperature higher than 500°C for 8 hours in air. The prepared catalyst was divided to physically admix with  $\text{SiO}_2$  and MgO in a weight ratio of 1:1.

### B. Catalyst Characterization

The surface structure of tungsten oxide species was investigated by FT-Raman spectrometer, NXR FT-Raman model, from Thermo Scientific. The Raman spectra of the samples were collected at ambient temperature with 50 mW power of laser. A scanning range of 300-1,200  $\text{cm}^{-1}$  with a resolution of 16  $\text{cm}^{-1}$  was applied. UV-vis diffuse reflectance spectra were compiled on Lambda 650 UV-vis spectrometer in the range of wavelength 200-800 nm at ambient temperature. The crystallite phase of catalyst was examined by X-ray diffraction, XRD (Siemens D5000) using Ni filter  $\text{Cu K}\alpha$  radiation. The amount of coke formation was measured by the temperature programmed oxidation, TPO. The  $\text{WO}_x/\text{SiO}_2$  spent catalysts were separated from  $\text{SiO}_2$  and MgO and then were contained into the reactor under the flow of 1%  $\text{O}_2$  in He and heated with the heat rate of 5°C•min<sup>-1</sup> until the temperature reached 700°C. The result was analyzed by the Agilent 7820A GC.

### C. Reaction Conditions

The reaction was carried out in a continuous flow, vertical fixed-bed reactor using trans-2-butene and ethylene as feed. The mixed catalysts were pretreated under  $\text{N}_2$  flow at temperature higher than 500°C in reactor for 1 hour. The reaction was operated at temperature 450°C and atmospheric pressure. The reaction products were analyzed online by GC Shimadzu 2014.

## III. RESULT AND DISCUSSION

The  $\text{WO}_x/\text{SiO}_2$  catalysts physically mixed with  $\text{SiO}_2$  and MgO were characterized by Raman spectroscopy, UV-vis spectrometer, X-rays diffraction and temperature programmed oxidation technique. The mixed catalysts were pretreated in  $\text{N}_2$  for 1 hours and then the  $\text{WO}_x/\text{SiO}_2$  catalysts were separated from  $\text{SiO}_2$  and MgO to analyze. Generally, the Raman band about 970  $\text{cm}^{-1}$  was attributed to the symmetric W=O stretching of tetrahedral tungsten oxide species which was suggested to an active site of metathesis reaction and the Raman band about 805  $\text{cm}^{-1}$  was attributed to the symmetric W-O stretching which referred to the tungsten oxide crystalline, suggested to non-active site [15]. Fig. 1 showed the Raman spectra of  $\text{WO}_x/\text{SiO}_2$  catalysts which were

separated from SiO<sub>2</sub> and MgO. The result showed that the Raman spectra of WO<sub>x</sub>/SiO<sub>2</sub> catalyst which physically mixed with MgO was similar to the Raman spectra of WO<sub>x</sub>/SiO<sub>2</sub> catalyst which physically mixed with SiO<sub>2</sub>, indicating that additional of MgO into the WO<sub>x</sub>/SiO<sub>2</sub> catalyst could not change the active site and the non-active site of metathesis reaction.

UV-vis is utilized to discriminate the structure of tungsten species for WO<sub>x</sub>/SiO<sub>2</sub> catalyst with SiO<sub>2</sub> and MgO. The UV-vis spectra of separated WO<sub>x</sub>/SiO<sub>2</sub> catalysts were exhibited in Fig. 2. There were three diffraction peaks at about 230, 300 and 400 nm, which were assigned to W<sup>6+</sup> (isolated WO<sub>4</sub><sup>2-</sup> tetrahedral species), W<sup>6+</sup> (distorted tetrahedral WO<sub>4</sub><sup>2-</sup> or octahedral polytungstate species) and WO<sub>3</sub> crystal, respectively [3], [15]. From Fig. 2, it seemed to be the same, revealing that the structure of tungsten species was unchangeable.

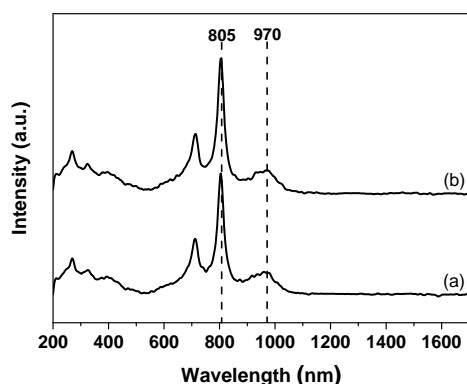


Fig. 1 Raman spectra of separated WO<sub>x</sub>/SiO<sub>2</sub> catalysts: (a) WO<sub>x</sub>/SiO<sub>2</sub> separated from SiO<sub>2</sub>, (b) WO<sub>x</sub>/SiO<sub>2</sub> separated from MgO

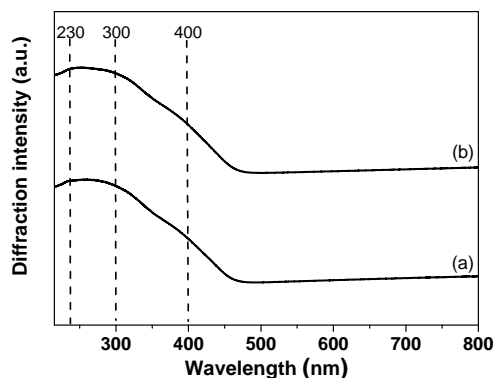


Fig. 2 UV-vis spectra of separated WO<sub>x</sub>/SiO<sub>2</sub> catalysts: (a) WO<sub>x</sub>/SiO<sub>2</sub> separated from SiO<sub>2</sub>, (b) WO<sub>x</sub>/SiO<sub>2</sub> separated from MgO

X-rays diffraction shows tungsten oxide crystallization. There were peaks at 2θ degrees = 23.12°, 23.60° and 24.38°, corresponding orthorhombic tungsten oxide crystallization [16]. The XRD pattern of WO<sub>x</sub>/SiO<sub>2</sub> catalysts which were separated from SiO<sub>2</sub> and MgO was shown in Fig. 3. It showed that physically mixed with MgO into WO<sub>x</sub>/SiO<sub>2</sub> catalyst was not affected on crystallization of tungsten oxide. From the

characterization of Raman spectroscopy, UV-vis spectrometer and X-rays diffraction, they could imply that the mixed MgO do not modify the surface and bulk structures of the WO<sub>x</sub>/SiO<sub>2</sub> catalyst.

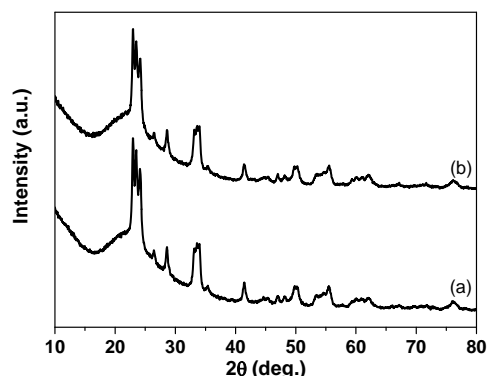
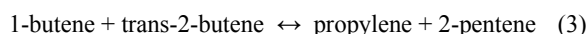
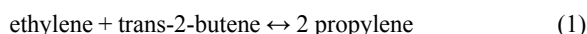


Fig. 3 XRD pattern of separated WO<sub>x</sub>/SiO<sub>2</sub> catalysts: (a) WO<sub>x</sub>/SiO<sub>2</sub> separated from SiO<sub>2</sub>, (b) WO<sub>x</sub>/SiO<sub>2</sub> separated from MgO

The WO<sub>x</sub>/SiO<sub>2</sub> catalyst physically mixed with MgO in the weight ratio 1:1 was investigated on the reaction of trans-2-butene and ethylene. The WO<sub>x</sub>/SiO<sub>2</sub> catalyst can occur both metathesis and double bond isomerization reaction [12], [17]. The tetrahedral coordinated tungsten oxide species should be the active centers for metathesis, while acid sites on surface of catalyst should be active centers for double bond isomerization [13]. For MgO, it could catalyze only double bond isomerization [18]. When it was physically mixed with the WO<sub>x</sub>/SiO<sub>2</sub> catalyst, the reaction between trans-2-butene and ethylene to propylene (olefins metathesis) cannot exist on MgO [14]. The possible reaction pathways of the WO<sub>x</sub>/SiO<sub>2</sub> catalyst which physically mixed with MgO were shown in (1)-(3):



The conversion of trans-2-butene and the selectivity of product distribution were shown in Table I. The WO<sub>x</sub>/SiO<sub>2</sub> catalyst physically admixed with MgO could improve conversion when compared to physically mix with SiO<sub>2</sub> because of the isomerization reaction on MgO. The trans-2-butene reactant in feed came into the reactor could contact both WO<sub>x</sub>/SiO<sub>2</sub> catalyst and MgO at the same time. Some part of trans-2-butene and ethylene could adsorb on WO<sub>x</sub>/SiO<sub>2</sub> catalyst occurred mainly metathesis reaction according to (1). Some part of trans-2-butene could also adsorb on MgO occurred isomerization reaction as follow in (2), suggesting the conversion of trans-2-butene would increase. In addition, the selectivity of propylene would be higher when the WO<sub>x</sub>/SiO<sub>2</sub> catalyst physically mixed with MgO because of cross metathesis between 2-butene and 1-butene which

occurred following by the isomerization reaction of trans-2-butene to 1-butene and then 1-butene reacted with 2-butene to produce propylene and 2-pentene as shown in (3). The same increasing trend of 2-pentene selectivity compared to propylene selectivity in the  $WO_x/SiO_2$  catalyst physically mixed with MgO helped confirm that additional propylene could be produced from the cross metathesis between 2-butene and 1-butene.

TABLE I  
PRODUCT DISTRIBUTION OF  $WO_x/SiO_2$  CATALYSTS PHYSICALLY MIXED WITH  $SiO_2$  AND MgO.

Catalyst	$WO_x/SiO_2 + SiO_2$	$WO_x/SiO_2 + MgO$
Conversion (%)	56.53%	60.47%
Selectivity (%)		
propylene	2.72%	4.01%
1-butene	42.97%	41.79%
iso-butene	0.38%	0.89%
cis-2-butene	51.88%	50.59%
2-pentene	1.58%	2.31%
$C_5+$	1.75%	2.62%

For coke formation on  $WO_x/SiO_2$  catalysts, the spent  $WO_x/SiO_2$  catalysts were separated from  $SiO_2$  and MgO. The coke formation on the spent metathesis catalysts was measured by TPO technique. The result was shown in Table II. The amount of coke that deposited on the  $WO_x/SiO_2$  catalysts when physically mixed with  $SiO_2$  and MgO were 0.02% and 0.07%, respectively. It showed that the coke formation on the  $WO_x/SiO_2$  catalysts when physically mixed with MgO was higher than the  $WO_x/SiO_2$  catalyst when physically mixed with  $SiO_2$ .

TABLE II  
AMOUNT OF COKE ON  $WO_x/SiO_2$  CATALYSTS PHYSICALLY MIXED WITH  $SiO_2$  AND MgO.

Catalyst	Amount of Coke (%)
$WO_x/SiO_2 + SiO_2$	0.02%
$WO_x/SiO_2 + MgO$	0.07%

In TPO profile, as illustrate in Fig. 4, there were two peaks of coke. The weak coke and hard coke took place at about 330°C and 480°C, respectively. The weak coke existed when the catalyst only physically mixed with MgO whereas the hard coke occurred both physically mixed with  $SiO_2$  and MgO. When we compared the amounts of coke formation on  $WO_x/SiO_2$  spent catalyst which separated from MgO to  $WO_x/SiO_2$  spent catalyst which separated from  $SiO_2$ , it was found that the  $WO_x/SiO_2$  catalyst physically admixed with MgO not only increased the conversion of trans-2-butene but also elevated the amount of coke formation on the catalyst. The coke deposition on  $WO_x/SiO_2$  spent catalyst physically mixed with MgO was higher than the catalyst which physically mixed with  $SiO_2$ , indicating that adding MgO could increase the coke precursor since MgO could catalyze isomerization reaction of undesired product to coke precursor and then the coke precursor would deposit on the acid site of  $WO_x/SiO_2$  catalyst as weak coke, behaving in the first peak of

TPO profile. The MgO contributed the isomerization reaction of 2-butene to 1-butene, then the 1-butene reacted with 2-butene to form propylene and 2-pentene. Many researches mentioned that the isomerization reaction is a cause of coke precursor formation [19], so we could postulate that some 2-pentene would consecutively react isomerization reaction to form coke precursor and deposit on catalyst as weak coke.

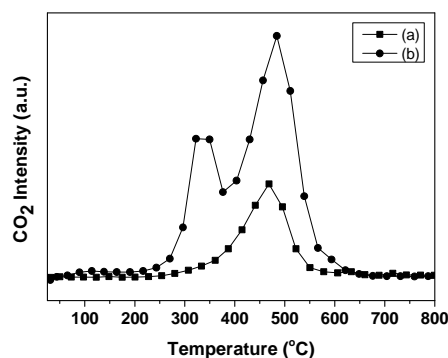


Fig. 4 TPO Profile of separated  $WO_x/SiO_2$  catalysts: (a)  $WO_x/SiO_2$  separated from  $SiO_2$ , (b)  $WO_x/SiO_2$  separated from MgO

#### IV. CONCLUSION

The additional MgO plays the important roles in the activity and coke formation on  $WO_x/SiO_2$  catalysts. It not only enhanced the conversion of trans-2-butene because of isomerization reaction but also increased the amount of coke deposit on the catalyst, suggesting that the coke precursor could be produced by isomerization reaction of undesired product and deposit on catalyst as weak coke.

#### ACKNOWLEDGMENT

The authors acknowledge Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for financial support.

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