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

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***Abstract*—**The effect of additional magnesium oxide (MgO) was investigated by using the tungsten oxide supported on silica catalyst (WO_x/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 WO_x/SiO_2 catalyst. The TPO profile presented two peaks when the WO_x/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.

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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 WO_x/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 WO_x/SiO_2 was prepared by incipient wetness impregnation method [6], [11]-[13], [15], [16]. The 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 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 cm^{-1} with a resolution of 16 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 Cu Kα radiation. The amount of coke formation was measured by the temperature programmed oxidation, TPO. The WO_x/SiO_2 spent catalysts were separated from SiO_2 and MgO and then were contained into the reactor under the flow of 1% O_2 in He and heated with the heat rate of 5°C•min^{-1} 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 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 WO_x/SiO_2 catalysts physically mixed with 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 N_2 for 1 hours and then the WO_x/SiO_2 catalysts were separated from SiO_2 and MgO to analyze. Generally, the Raman band about 970 cm^{-1} was attributed to the symmetric W=O stretching of tetrahedral tungsten oxide spices which was suggested to an active site of metathesis reaction and the Raman band about 805 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 WO_x/SiO_2 catalysts which were

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separated from SiO_2 and MgO. The result showed that the Raman spectra of WO_x/SiO_2 catalyst which physically mixed with MgO was similar to the Raman spectra of WO_x/SiO_2 catalyst which physically mixed with SiO_2, indicating that additional of MgO into the WO_x/SiO_2 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_x/SiO_2 catalyst with SiO_2 and MgO. The UV-vis spectra of separated WO_x/SiO_2 catalysts were exhibited in Fig. 2. There were three diffraction peaks at about 230, 300 and 400 nm, which were assigned to W^{6+} (isolated WO_4^{2-} tetrahedral species), W^{6+} (distorted tetrahedral WO_4^{2-} or octahedral polytungstate species) and WO_3 crystal, respectively [3], [15]. From Fig. 2, it seemed to be the same, revealing that the structure of tungsten species was unchangeable.

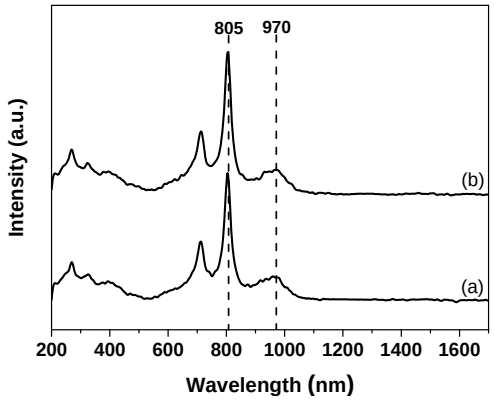


Fig. 1 Raman spectra of separated WO_x/SiO_2 catalysts: (a) WO_x/SiO_2 separated from SiO_2, (b) WO_x/SiO_2 separated from MgO

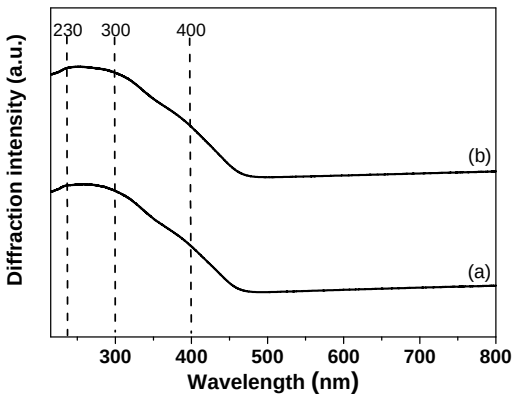


Fig. 2 UV-vis spectra of separated WO_x/SiO_2 catalysts: (a) WO_x/SiO_2 separated from SiO_2, (b) WO_x/SiO_2 separated from MgO

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_x/SiO_2 catalysts which were separated from SiO_2 and MgO was shown in Fig. 3. It showed that physically mixed with MgO into WO_x/SiO_2 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_x/SiO_2 catalyst.

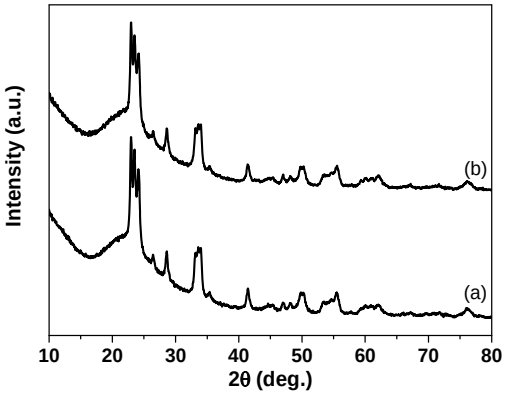


Fig. 3 XRD pattern of separated WO_x/SiO_2 catalysts: (a) WO_x/SiO_2 separated from SiO_2, (b) WO_x/SiO_2 separated from MgO

The WO_x/SiO_2 catalyst physically mixed with MgO in the weight ratio 1:1 was investigated on the reaction of trans-2-butene and ethylene. The WO_x/SiO_2 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_x/SiO_2 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_x/SiO_2 catalyst which physically mixed with MgO were shown in (1)-(3):

$$\text{ethylene} + \text{trans-2-butene} \leftrightarrow 2\ \text{propylene} \quad (1)$$

$$\text{trans-2-butene} \leftrightarrow \text{1-butene} \quad (2)$$

$$\text{1-butene} + \text{trans-2-butene} \leftrightarrow \text{propylene} + \text{2-pentene} \quad (3)$$

The conversion of trans-2-butene and the selectivity of product distribution were shown in Table I. The WO_x/SiO_2 catalyst physically admixed with MgO could improve conversion when compared to physically mix with SiO_2 because of the isomerization reaction on MgO. The trans-2-butene reactant in feed came into the reactor could contact both WO_x/SiO_2 catalyst and MgO at the same time. Some part of trans-2-butene and ethylene could adsorb on WO_x/SiO_2 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_x/SiO_2 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 confirmly 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.

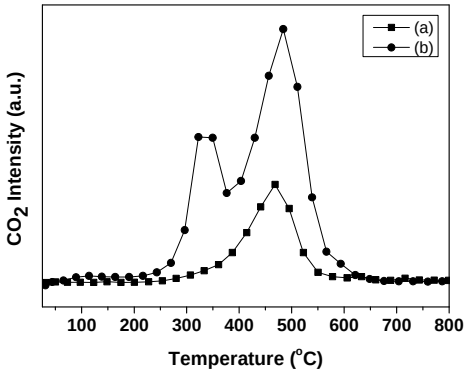


Fig. 4 TPO Profile of separated WO_x/SiO_2 catalysts: (a) WO_x/SiO_2 separated from SiO_2, (b) WO_x/SiO_2 separated from MgO

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.

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