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Article

Metathesis of Ethylene and *Trans*-2-Butene over MgO Admixed WO_3/SiO_2 Catalysts

Prinyanee Suttibut, Piyasan Praserthdam, and Joongjai Panpranot*

Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
*E-mail: joongjai.p@chula.ac.th (Corresponding author)

Abstract. The performances of MgO admixed WO_3/SiO_2 catalysts were investigated in the cross metathesis of ethylene and 2-butene to propylene at 450°C atmospheric pressure. Compared to the WO_3/SiO_2 + silica gel, the conversion of 2-butene and the propylene selectivity were much higher on all the WO_3/SiO_2 + MgO catalysts. An increased propylene yield corresponded to the decrease in 1-butene and *cis*-2-butene by products. The results in this study also suggest suitable method to prepare highly stable MgO catalysts in order to maximize the propylene yield.

1. Introduction

Due to the highly demanded propylene in the market, the cross metathesis of ethylene and 2-butene to propylene is of a great interest for both academia and industry [1, 2]. Among the most successful heterogeneous olefin metathesis catalysts including Mo, W, and Re in oxide form supported on high surface area inorganic oxides such as silica and alumina, the W-based catalysts receive much more attention for commercial use due to their long lifetime, considerable resistance to poisoning and low price [3, 4]. However, because they are active at relatively high reaction temperature, side reactions and lower selectivity are inevitable. In addition, the catalyst performances are often dependent on the metal precursor, the preparation method, and modification of the supports [4, 5].

During the metathesis of ethylene and 2-butene, 1-butene in feedstock can interfere ethylene and 2-butene metathesis by competitively metathesizing with 2-butene resulting in higher molecular weight hydrocarbon formation as a by-product. In order to avoid this by-product formation, double-bond isomerization catalysts, such as magnesium oxide (MgO), may be used to isomerize 1-butene to 2-butene as 2-butene is consumed in the reaction [6]. According to the US patent number 8,586,813 (2013) [6], MgO catalysts may be mixed with metathesis catalysts for performing both double-bond isomerization and metathesis in the same reactor. MgO is a particularly preferred basic isomerization catalyst. It is expected that a double-bond isomerization catalyst can convert 1-butene to 2-butenes during the metathesis reaction, thus increase the propylene yield of the metathesis reaction [7].

Typically, MgO contains numerous basic sites of various strength (strong: low coordination O^{2-} anions, medium: oxygen in Mg^{2+}–O^{2-} pairs, and weak: surface OH^- groups. The isomerization activity of MgO, however, has often been found to be related to the presence of some specific low coordinated sites such as step, edge, and corner sites. A recent study from our group showed that rearrangement of the MgO structure occurred upon N_2 pretreatment at 325°C followed by isomerization reaction at 125°C [8]. Thus, it is interesting to investigate how the restructuring of MgO catalysts may affect the performances of the MgO admixed with W-based catalysts in the metathesis reaction.

In the present work, MgO catalysts, which were prepared by co-precipitation, solvothermal, and sol-gel methods, were physically mixed with the 9 wt% WO_3/SiO_2 catalysts and tested in the cross metathesis of ethylene and 2-butene for propylene production in a single catalyst bed reactor. The physicochemical properties of MgO were characterized by means of X-ray diffraction (XRD), N_2 physisorption, Fourier-transformed infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and basicity titration. The catalytic activity, propylene yield, and product distribution of metathesis reaction were correlated to the reactivity and characteristics of the MgO co-catalysts, which depended on the preparation protocols used.

2. Experimental

2.1. Synthesis of MgO Catalysts

The MgO catalysts were prepared by three different routes namely co-precipitation (CP), sol-gel (SG), and solvothermal (SV) using magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) (Ajax Finechem) and potassium hydroxide (KOH) (AnalaR) as the starting materials. For the CP method, firstly, 0.8 M of $Mg(NO_3)_2.6H_2O$ and 0.9 M of KOH solutions were prepared in de-ionized water. These two solutions were added dropwise into 200 cm^3 of deionized water under vigorous stirring. The pH was controlled at 11-12. The complete solution was separated by centrifuging and washed in de-ionized water. The wet white solid was dried in ambient air overnight at 80°C and then calcined at 500°C for 4 h in air.

The MgO catalysts were prepared by SG according to the procedure described in Tamilselvi et al. [9]. Firstly, 0.2 M $Mg(NO_3)_2 \cdot 6H_2O$ was dissolved in de-ionized water then 0.4 M NaOH was added dropwise under sonication and mixed at room temperature for 2 h. The precipitation formed was washed by de-ionized water and followed by ethanol. After that the wet solid was dried at 110°C for 24 h. Finally, the white solid was calcined at 500°C for 4 h in air. The procedure described by Hadia et al. [10] was employed for the preparation of MgO catalysts by the SV method. The solvent containing ethanol and water was firstly prepared in equal volume ratio. Then 6 g of NaOH were added to 70 cm^3 of the mixed solvent and stirred until completely mixed. 3.446 g of $Mg(NO_3)_2 \cdot 6H_2O$ were added to the solution and stirred vigorously. Then the white precipitate was transferred to an autoclave chamber and placed inside a

pretreated oven at 180°C for 10 h. The precipitation formed was filtered and washed by de-ionized water and followed by ethanol. After that the wet solid was dried at 80°C for 2 h. Finally, the white solid was calcined at 500°C for 4 h in air. The MgO catalysts prepared by CP, SG, and SV methods are denoted as MgO(CP), MgO(SG), and MgO(SV), respectively.

2.2. Synthesis of WO₃/SiO₂ Catalysts

The WO_3/SiO_2 catalysts with 9 wt% tungsten loading were prepared by the incipient wetness impregnation of an aqueous solution of ammonium metatungstate hydrate (Aldrich) over silica gel (Aldrich, Davisil grade 646). The catalysts were dried at room temperature for 2 h and 110°C for overnight. Finally, the white solid was calcined in a tubular furnace at 500°C for 4 h in air to remove any residue.

2.3. Catalyst Characterization

The XRD patterns of catalysts were obtained using a Bruker D8 Advance X-ray diffractometer, with CuK_α radiation and a Ni filter in 10-80° 2θ angular region. The BET surface area, pore size, and pore volume of the catalysts were calculated by N_2 physisorption using a Quadrasorb evo (QDS-30) automated system. The functional groups on catalyst surface were identified by FT-IR using a Nicolet 6700™ spectrometer in the range of 400-1000 cm^{-1} and 3200-3800 cm^{-1}. The weight loss of catalysts was measured by thermal gravimetric analysis (TGA) using a SDT Q6000. SEM micrographs of catalysts were obtained with a Hitachi S3400N scanning electron microscope. The amounts of basic sites were measured by titration technique according to the procedure explained by Pokrovsky et al. [11].

2.4. Reaction Study

The isomerization of 1-butene was carried out in a stainless steel flow reactor at 325°C and atmospheric pressure. Feed gas was composed of 10% 1-butene in nitrogen (Linde PLC, Thailand). Approximately 1.5 g of the MgO catalyst was packed in the reactor. The feed gas flowrate was 12 cm^3min^{-1} with the gas hourly space velocity (GHSV) 231 h^{-1}. Before the reaction tests, the MgO catalysts were pretreated at 325°C under continuous flow of N_2 (ultra-high purity from Linde (Thailand) PLC) with flow rate 30 cm^3/min for 1 h. The products were analyzed by Agilent 7820A online gas chromatography equipped with FID detector.

The metathesis of *trans*-2-butene and ethylene was carried out in the same reactor at 450°C and atmospheric pressure. The reaction was conducted for 5 h. Feed gas was composed of 2% *trans*-2-butene and excess of ethylene in nitrogen provided by Linde (Thailand) PLC. Approximately 1.5 g of the MgO catalyst and 1.5 g of WO_3/SiO_2 were physical mixed and then were packed in the reactor. The feed gas flow rate was 12 cm^3/min with the gas hourly space velocity (GHSV) 257 h^{-1}. Before the reaction tests, the WO_3/SiO_2 + MgO mixed catalysts were pretreated at 450°C under continuous flow of N_2 (ultra-high purity from Linde (Thailand) PLC) with flow rate 30 cm^3/min for 1 h. The products were analyzed by Agilent 7820A online gas chromatography equipped with FID detector.

3. Results and Discussion

3.1. Physicochemical Properties of the As-Prepared MgO Catalysts

The physicochemical properties of the as-prepared MgO catalysts are shown in Table 1. Among the different preparation methods used in this study, the SV method produced nanocrystalline MgO with the largest BET surface area (102 m²/g). The surface area of the MgO obtained from the CP and SG methods were ranged between 72-88 m²/g. Despite their lower surface area, the MgO(SG) exhibited higher amount of basicity as measured by the titration technique. The XRD patterns of the prepared MgO catalysts are shown in Fig. 1. All the prepared catalysts exhibited only the MgO phase, which were apparent at 2θ degrees = 36.8°, 42.6°, 62.1°, 74.6°, and 78.4°. However, the average crystallite size of the MgO(SG) was much larger (23 nm) than those prepared by CP and SV methods (average crystallite size ~ 9 nm). The adsorption-desorption isotherms of the MgO catalysts are shown in Fig. 2. The MgO(CP) and MgO(SV) catalysts exhibited type IV isotherm with a hysteresis loop that associated with the mesoporous

characteristics whereas most of the pores in the MgO(SG) were macropores. The catalyst morphology is shown by the SEM micrographs in Fig. 3 as agglomeration of irregular aggregates.

The TGA measurements were carried out on the fresh catalysts after exposed in air at room temperature for 3 days and the results are shown Fig. 4. The weight loss of catalysts was found to be in the order: MgO(CP) 34.3% > MgO(SV) 24.3% > MgO(SG) 21.3%. The first region of weight loss occurred at 40ºC - 250ºC was attributed to the removal of the physisorbed water molecules. The major weight loss at around 250ºC - 450ºC was attributed to the decomposition of magnesium hydroxide to magnesium oxide. The decomposition of $Mg(OH)_2$ to form MgO was suggested to complete in the temperature region 500ºC - 680ºC [12].

Table 1. The BET surface area, pore volume, average pore size, average crystallite size, and basicity of MgO catalysts (based on XRD patterns and titration technique).

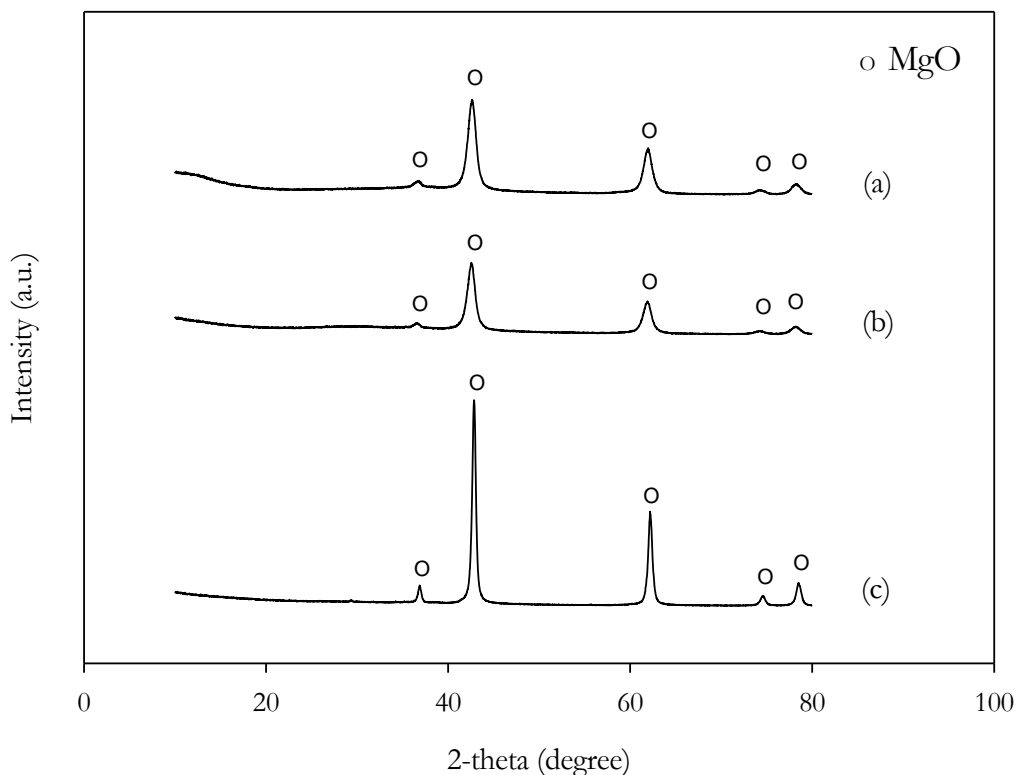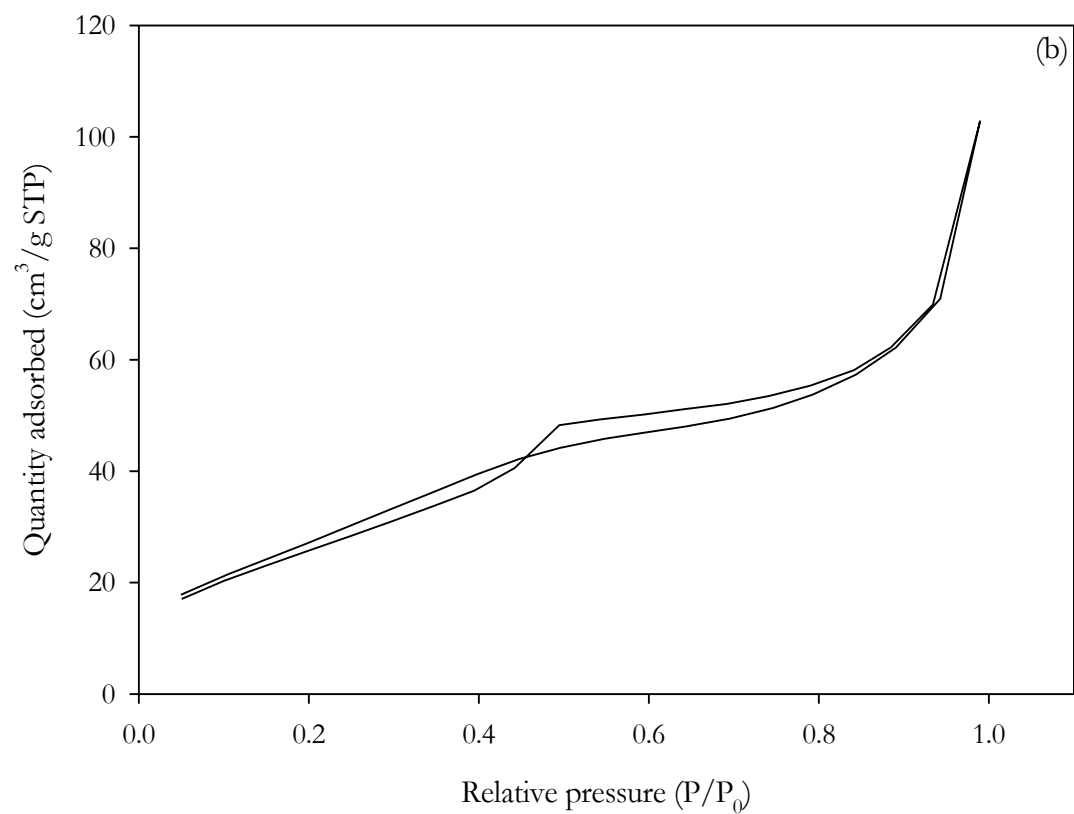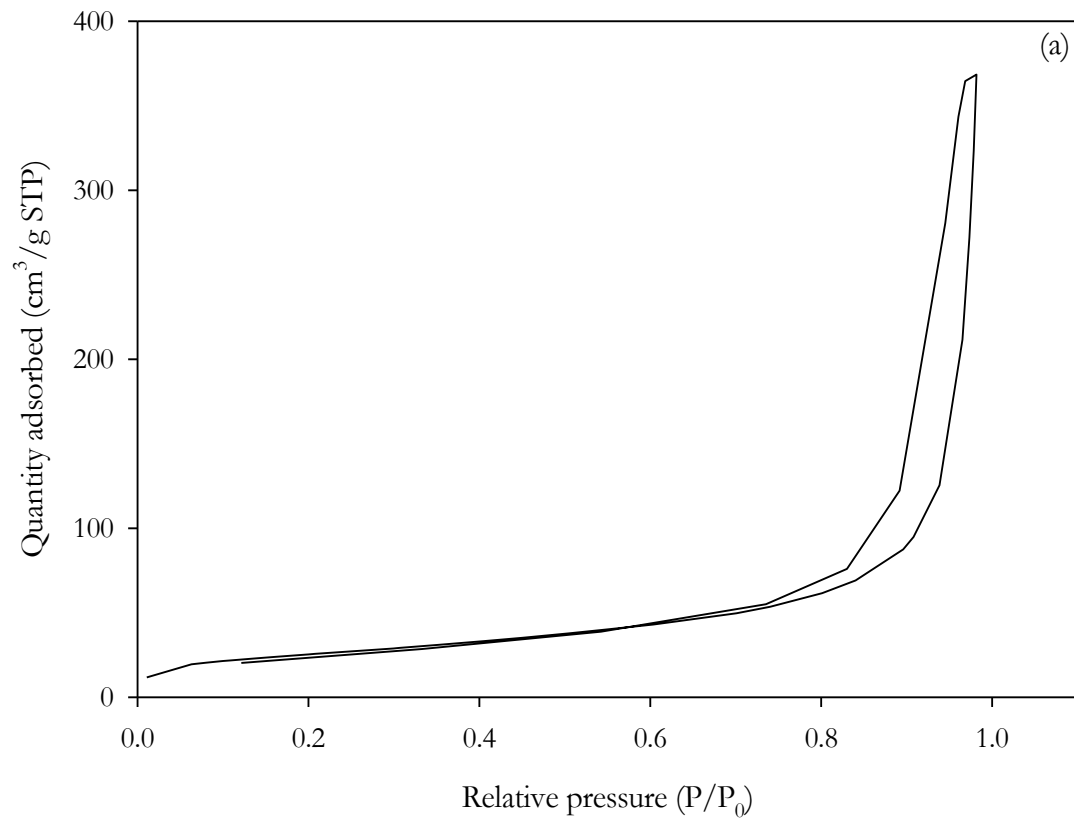| Catalyst	BET (m^2/g)	Pore volume (cm^3/g)	XRD crystallite size (nm)	Basicity titration $(\mu mol/g)$
Fresh Catalyst				
Fresh-MgO(CP)	88.1	0.6	MgO (8.6)	2000
Fresh-MgO(SV)	102	0.3	MgO (9.2)	2000
Fresh-MgO(SG)	71.6	1.7	MgO (22.9)	3000

Fig. 1. The XRD patterns of the as-prepared MgO catalysts: (a) MgO(CP); (b) MgO(SV); (c) MgO(SG).
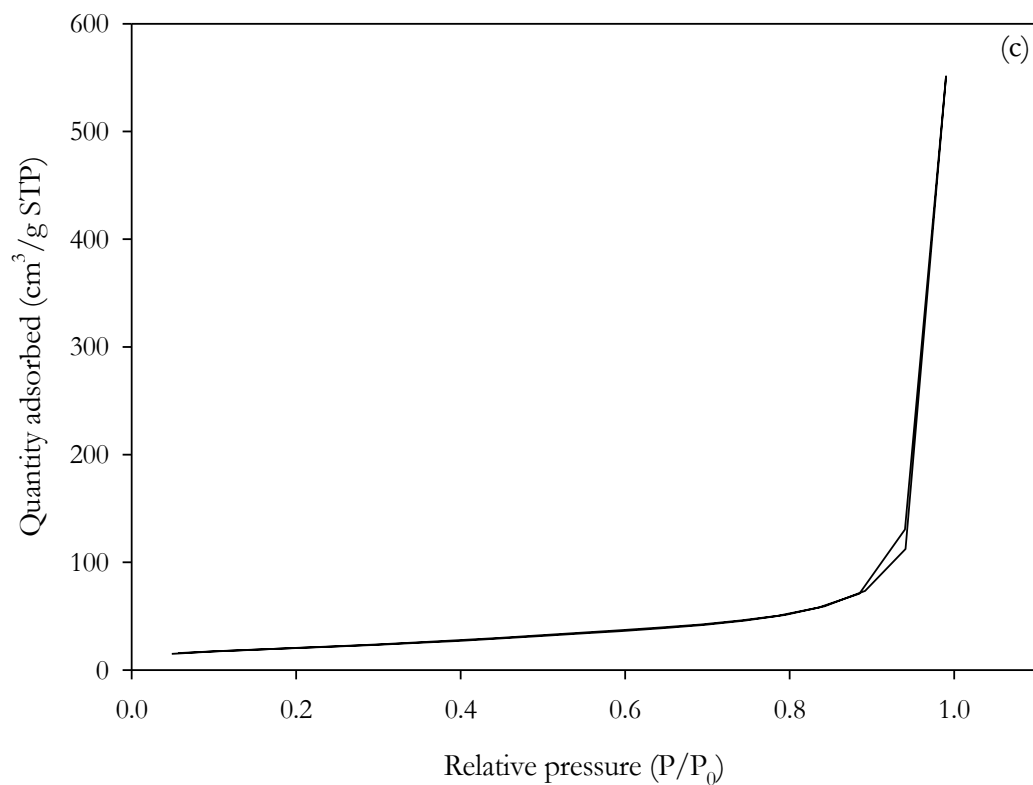
Fig. 2. The N_2 adsorption–desorption isotherm of the as-prepared MgO catalysts: (a) MgO(CP); (b) MgO(SV); (c) MgO(SG).
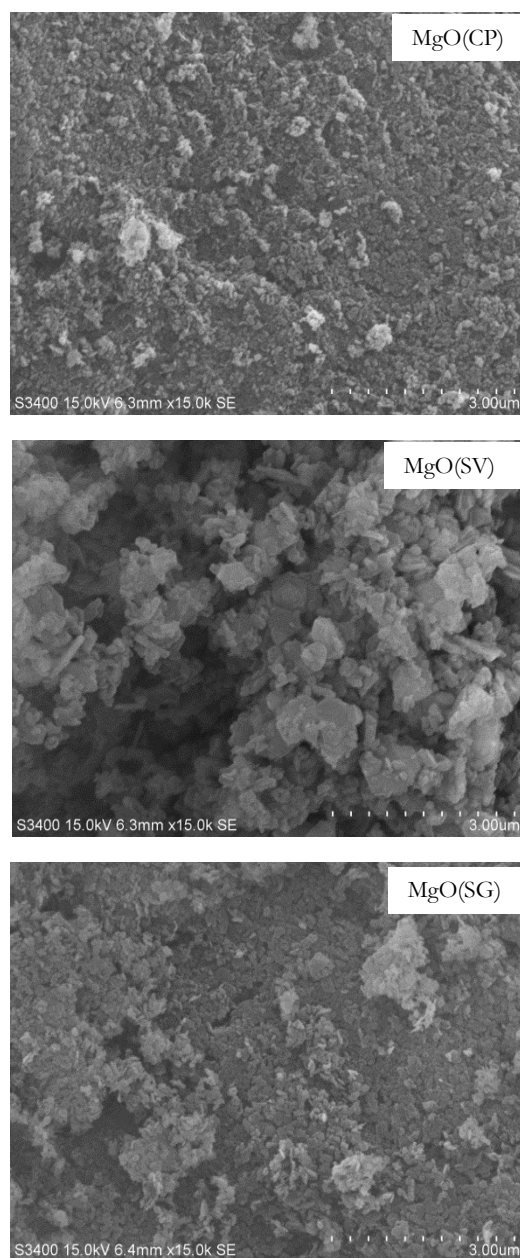
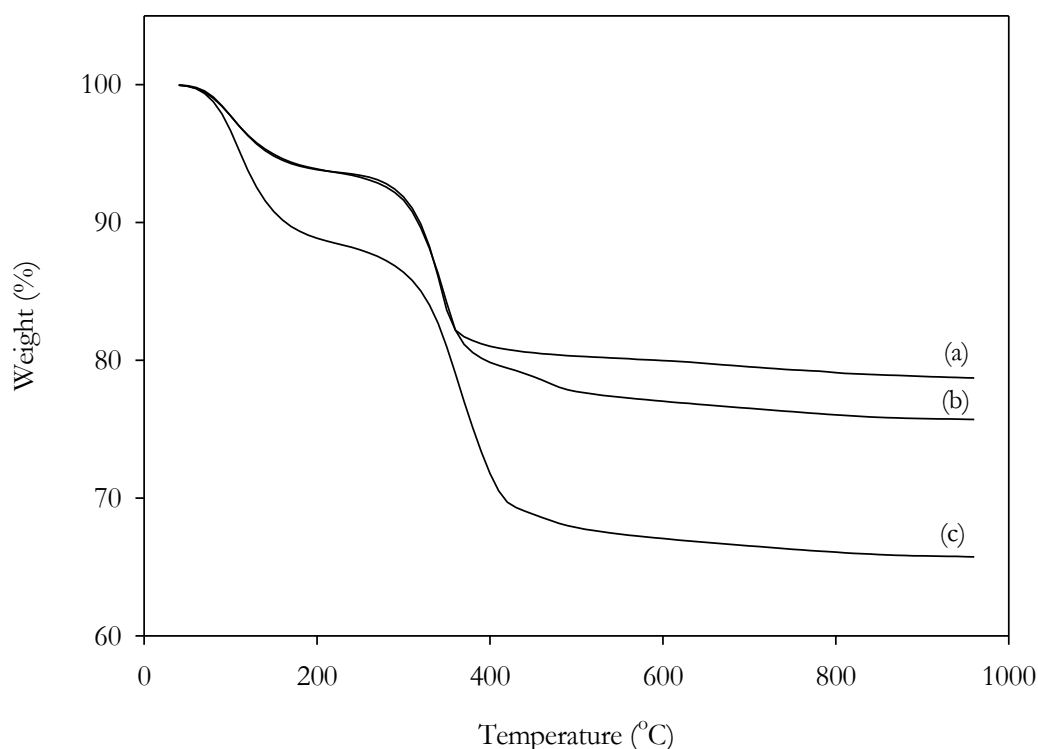Fig. 3.   The SEM micrographs of the as-prepared MgO catalysts.

Fig. 4. The TGA of fresh MgO catalysts after exposed in air at room temperature for 3 days: (a) fresh-MgO(SG)- RT 3 days; (b) fresh-MgO(SV)-RT 3 days; (c) fresh-MgO(CP)-RT 3 days.

3.2. Isomerization of 1-Butuene on MgO Catalysts

All the prepared MgO catalysts were tested in the isomerization of 1-butene to 2-butene at 325℃ and atmospheric pressure. The conversions of 1-butene and 2-butene selectivity as a function of reaction time obtained on the various MgO catalysts are shown in Fig. 5. All the MgO catalysts exhibited relatively high isomerization activity (1-butene conversion 77-79%) with 2-butene selectivity > 99%. From the characterization results, the isomerization activity may be correlated to the reactivity of the catalysts for OH adsorption (the TGA results). Such findings follow the more recent trend showing the dependence of MgO reactivity on the presence of specific low coordinated sites such as step, edge, and corner sites rather than on the total number of basic sites [13]. A correlation between the catalytic activity of MgO and the amount of OH groups has been reported by Chizallet et al. [14]. The catalytically active sites were identified as $O_{1C}H$ and $O_{2C}H$ formed by hydroxylation of the steps, corners and O^{2-}_{3C}-terminated kinks. A recent study by Petitjean et al. [15] also showed that the partial hydroxylated MgO catalyzed basic MBOH conversion better than the dehydroxylated MgO.
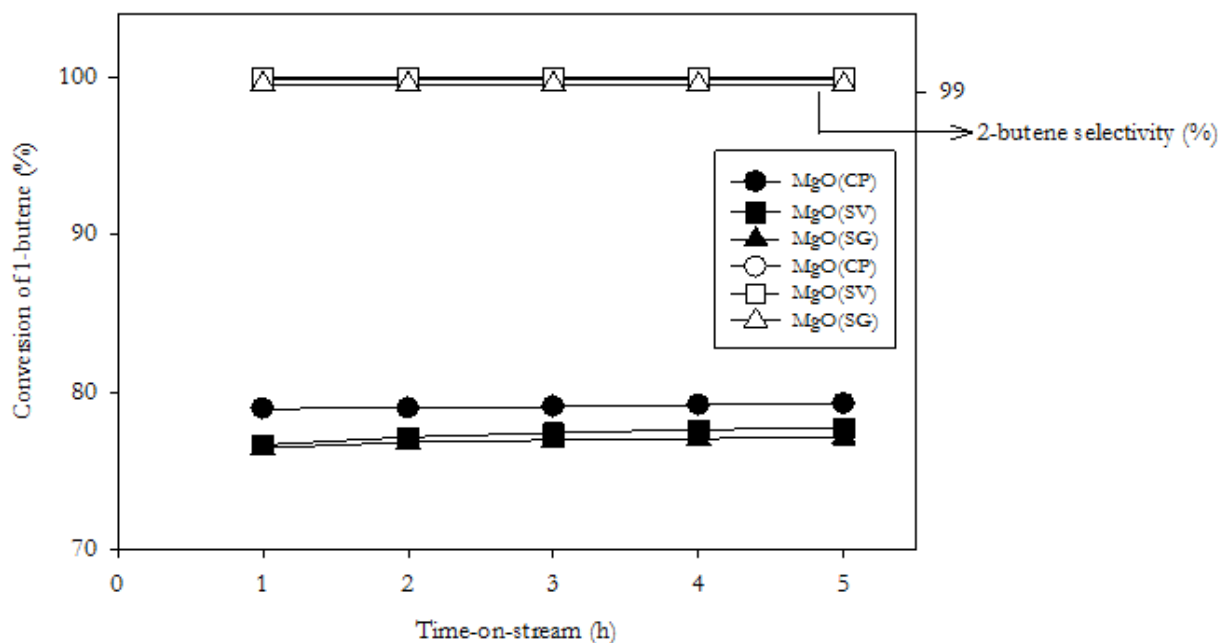
Fig. 5.   The results of 1-butene isomerization over MgO catalysts.

3.3. Restructuring of MgO Catalysts after 1-Butene Isomerization

The XRD patterns of the spent MgO catalysts after 1-butene isomerization at 325°C in comparison to the fresh ones are shown in Fig. 6. All the fresh catalysts contained only single phase MgO. There were no changes of the MgO phase on the fresh catalysts upon contact with moisture for 3 days. After the reaction tests, the spent catalysts were also left in air for 3 days. Additional peaks corresponding to the $Mg(OH)_2$ phase were observed at 2θ degrees = 18.3°, 37.8° , 50.8°, and 58.5° for the MgO(CP) and MgO(SV) whereas the MgO(SG) still exhibited only the single phase MgO. The OH groups of the $Mg(OH)_2$ structure were confirmed by the FT-IR results of the spent catalysts and the results are shown in Fig. 7. The peaks at wavenumber 3618, 3646, 3696, 3698, 3723 and 3726 cm^{-1} corresponded to OH groups of the $Mg(OH)_2$ structure [8]. For the MgO(CP) and MgO(SV), these OH peaks were higher for the spent catalysts compared to the fresh ones. This change was not observed for the MgO(SG) in which the spent catalysts showed relatively small OH peaks. There were no significant differences in the morphology between fresh and spent catalysts (not shown). Based on the characterization results from XRD, and FT-IR, it can be summarized that the MgO(CP) and MgO(SV) possessed strong OH adsorption sites whereas MgO(SG) contained weak adsorbed OH sites. According to Higashimoto et al. and Chizallet et al. [16, 17], OH formed on monoatomic steps, kinks, or divacancies are much more stable than those formed on higher steps and those formed on corners. It is also noted that the $Mg(OH)_2$ phase could not be reverse back to the single MgO phase by the same pretreatment used (N_2, 325°C, 1h).
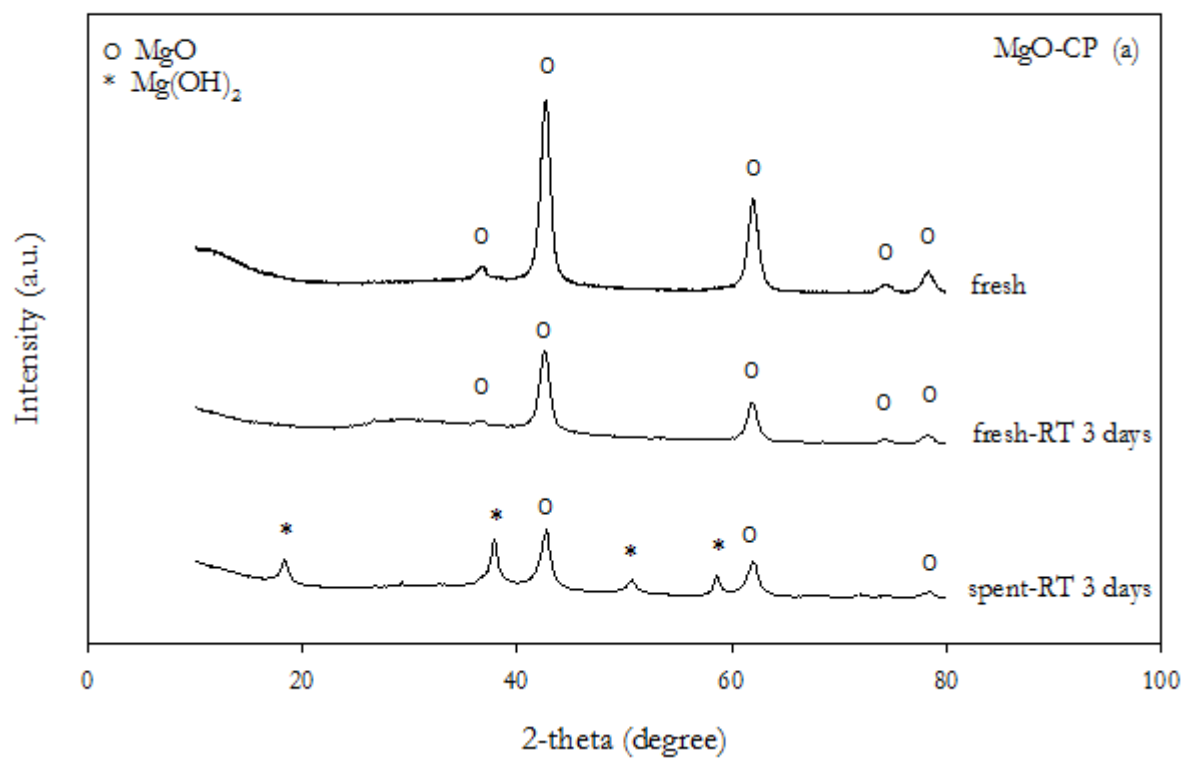
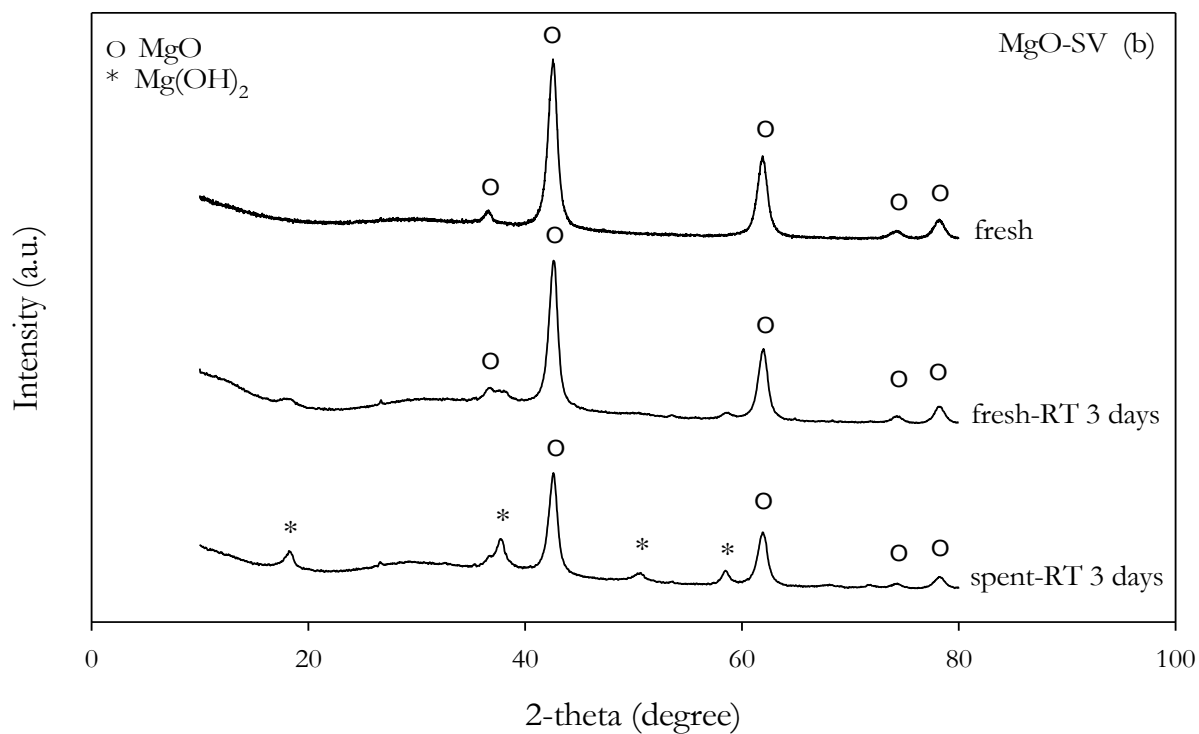Fig. 6(a)The XRD patterns of fresh and spent MgO(CP) catalysts.

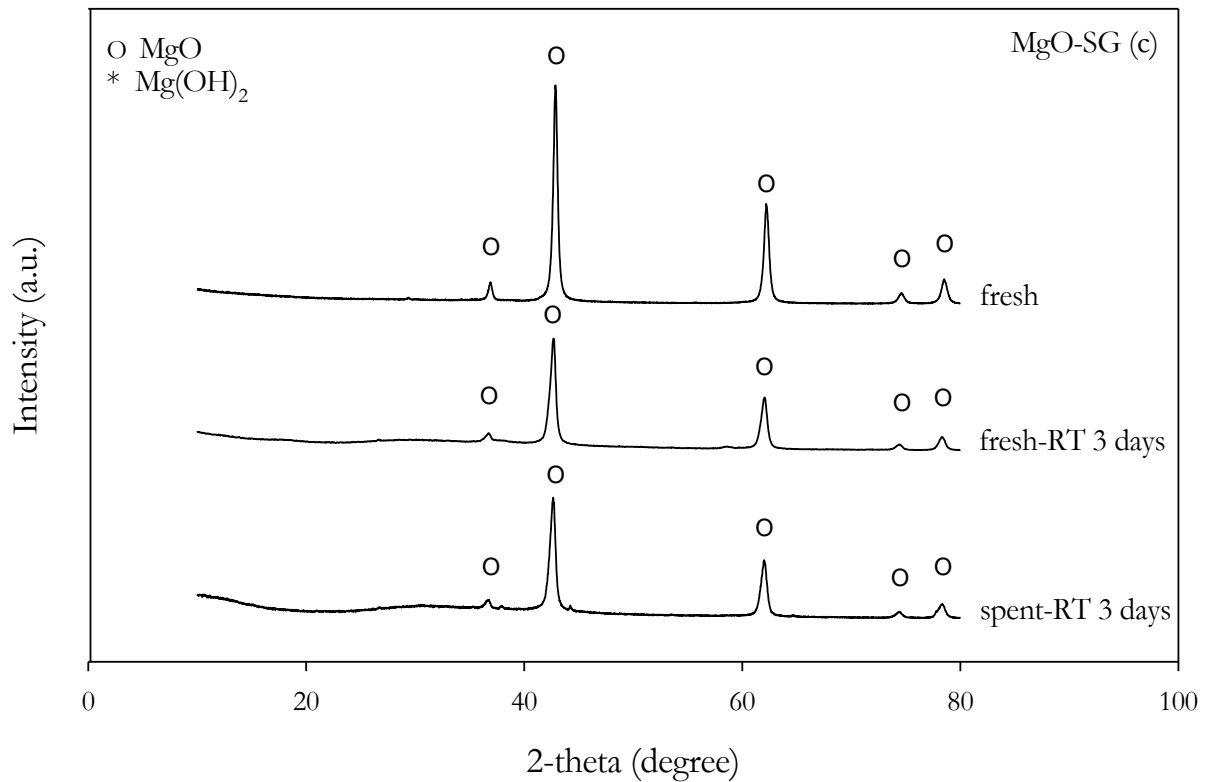Fig. 6(b)The XRD patterns of fresh and spent MgO(SV) catalysts.

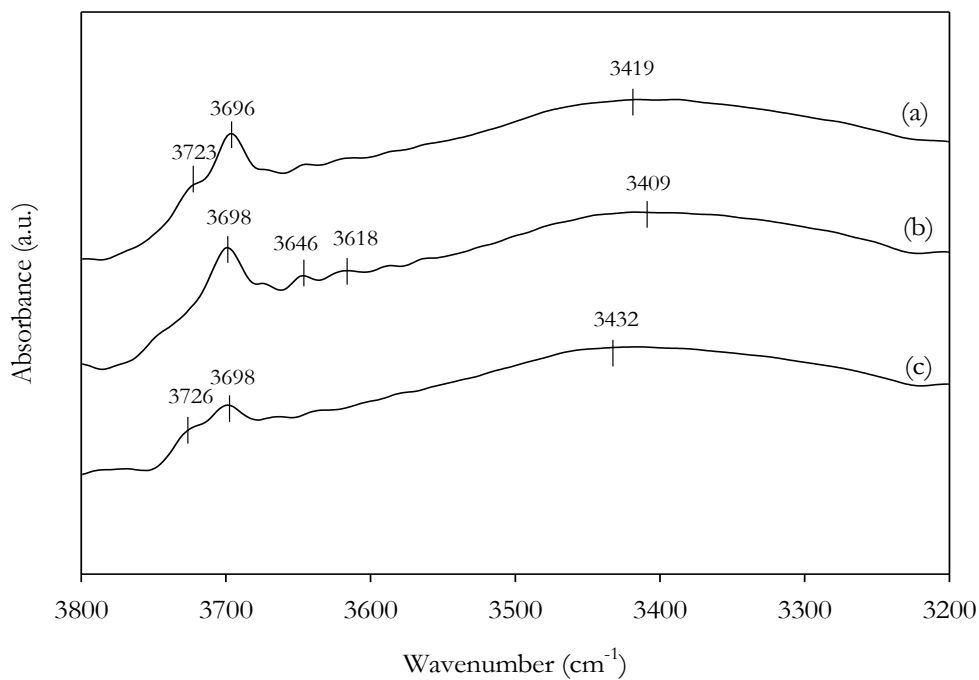Fig. 6(c) The XRD patterns of fresh and spent MgO(SG) catalysts.

Fig. 7. The FT-IR spectra of spent MgO catalysts (after isomerization tests) in the region 3200 - 3800 cm^{-1}: (a) spent-MgO(CP); (b) spent-MgO(SV); (c) spent-MgO(SG).

3.4. Metathesis of Ethylene and *Trans*-2-Butene on the Mixed WO₃/SiO₂+MgO Catalysts

The activity of the WO_3/SiO_2 physically mixed with MgO in the cross metathesis of ethylene and *trans*-2-butene are shown in Fig. 8. The WO_3/SiO_2 mixed with silica gel was employed for comparison purposes. It is clearly seen that the admixed MgO with the WO_3/SiO_2 (weight ratio 1:1) resulted in much higher conversion of *trans*-2-butene compared to the one physically mixed with silica gel along the 5 h reaction time. The *trans*-2-butene conversion was found to be varied in the order: WO_3/SiO_2 + MgO(SG) > WO_3/SiO_2 + MgO(SV) > WO_3/SiO_2 + MgO(CP) > WO_3/SiO_2 + silica gel. Despite their similar activity in 1-butene isomerization reaction, the WO_3/SiO_2 + MgO(CP) showed the lowest metathesis activity among the MgO admixed WO_3/SiO_2 catalysts. It is postulated that restructuring of the MgO during the reaction affected the catalyst performances in the metathesis of ethylene and 2-butene over the mixed WO_3/SiO_2 + MgO catalysts.
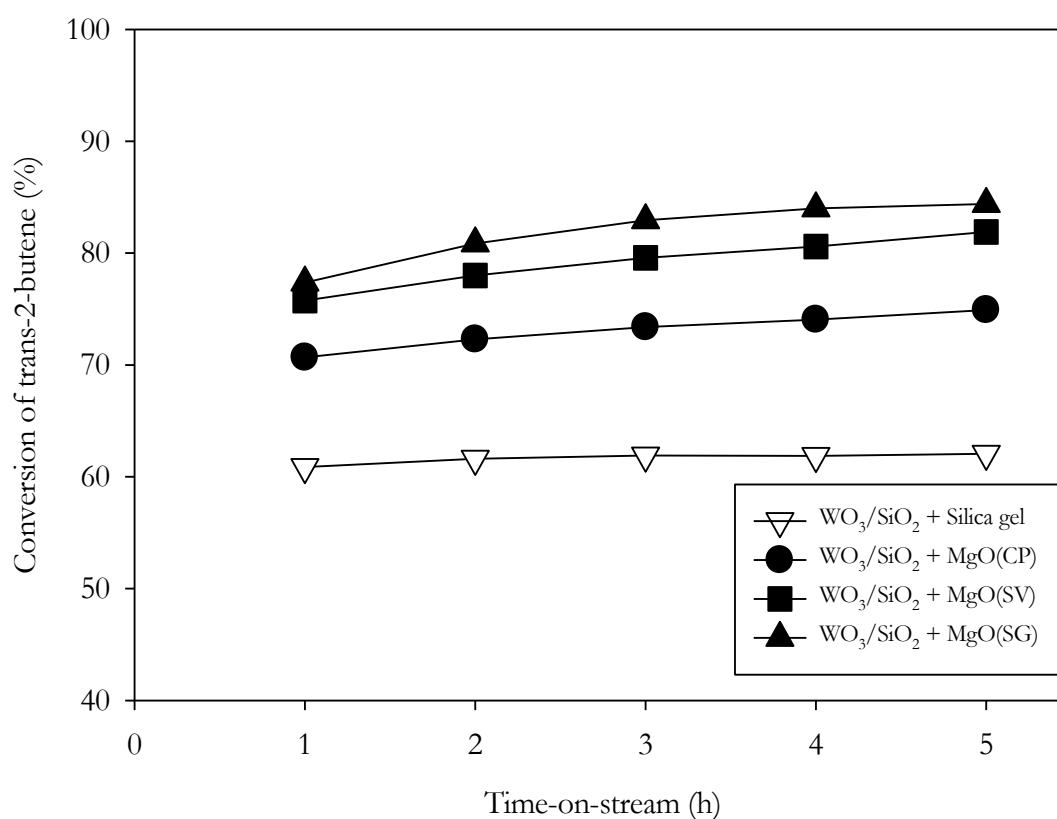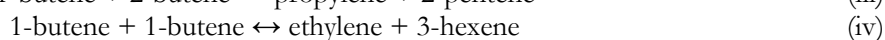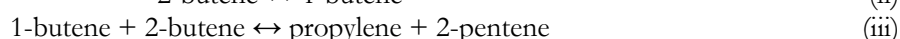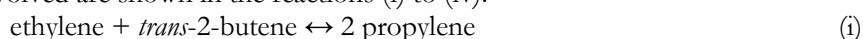

Fig. 8. The catalytic activity of the mixed WO_3/SiO_2 + MgO (or silica gel) catalysts in the cross metathesis of ethylene and *trans*-2-butene.

Generally, the performances of W-based catalysts in metathesis reaction depend on many factors such as the amount and the nature of active sites, the active site concentration and dispersion [4, 18]. Addition of extra supports including silica [19], TiO_2 and ZrO_2 [20] could provide more space for tungsten migration, resulting in a better dispersion of the tungsten oxide species so that the catalytic activity was enhanced. Nevertheless, the surface and bulk structures of the WO_3/SiO_2 catalysts in the present work were not altered when physically mixed with the MgO catalysts and tested in the metathesis of ethylene and 2-butene as confirmed in our previous work by the XRD, Raman, and UV-Vis spectroscopy [21]. Hu et al. also studied the metathesis of 1-butene and ethylene to propylene on the W-contained catalysts mixed with MgO [22]. It was confirmed that MgO did not catalyze the reaction of 2-butene and ethylene for propylene. The only role of MgO was to convert 1-butene to 2-butene.

However, in this study, pure *trans*-2-butene was used as the limiting reactant in addition to the excess ethylene. The main reactions involved are shown in the reactions (i) to (iv):

$$\text{ethylene} + \textit{trans}\text{-2-butene} \leftrightarrow 2 \text{ propylene} \tag{i}$$

$$\text{2-butene} \leftrightarrow \text{1-butene} \tag{ii}$$

$$\text{1-butene} + \text{2-butene} \leftrightarrow \text{propylene} + \text{2-pentene} \tag{iii}$$

$$\text{1-butene} + \text{1-butene} \leftrightarrow \text{ethylene} + \text{3-hexene} \tag{iv}$$

Besides the metathesis products, the products from isomerization reactions were observed including 1-butene, *cis*-2-butene, and iso-butene. The product distribution obtained from the mixed WO_3/SiO_2 + MgO (or silica gel) catalysts in terms of %selectivity and %yield after 5 h reaction time are summarized in Table 2 and Fig. 9, respectively. Compared to the mixed WO_3/SiO_2 + MgO, the WO_3/SiO_2 + silica gel exhibited lower conversion of *trans*-2-butene and much lower propylene selectivity with higher amounts of 1-butene and *cis*-2-butene. Therefore, the isomerization of *trans*-2-butene occurred as the side reactions without MgO catalysts on the isomerization sites of the WO_3/SiO_2 catalysts. The higher yields of these products after 5 h reaction suggests that the cross metathesis reactions between 1-butene and 2-butene or 1-butene self metathesis for additional propylene production proceeded much slower as compared to the main metathesis reaction between ethylene and 2-butene. It is also noticed that the isomerization sites on the WO_3/SiO_2 were not strong enough to convert 1-butene and *cis*-2-butene to *trans*-2-butene. However, in the presence of MgO co-catalysts, these by-products were converted back to *trans*-2-butene and additional propylene was mainly produced by the main metathesis reaction between *trans*-2-butene and excess ethylene (reaction (i)). The effect of *cis*/*trans*-2-butene isomers on the metathesis activity of WO_3/SiO_2 has been reported by Poovarawan et al. [23]. The conversion of 2-butene was found to be lower when the reactant feed contained the mixture of *cis*/*trans*-2-butene isomers, compared to the ones using pure *trans*-2-butene as the reactant feed. Furthermore, the metathesis reaction of 1-butene with ethylene is considered to be a non-productive reaction as the products of this metathesis reaction are essentially the same as reactants. Therefore, it is advantageous to convert as much of 1-butene to 2-butene, simultaneously during metathesis to maximize the production of propylene. Nevertheless, as revealed by the characterization results, there were strong and weak OH adsorption sites on the MgO catalysts. The superior performances of the mixed WO_3/SiO_2 + MgO catalysts in the metathesis of ethylene and 2-butene for propylene production suggest that MgO containing weak OH adsorption sites is more appropriate to use as the co-catalyst under the reaction conditions used.

Table 2. Catalytic performances of WO_3/SiO_2 physically mixed with MgO catalysts in the metathesis of ethylene and *trans*-2-butene.

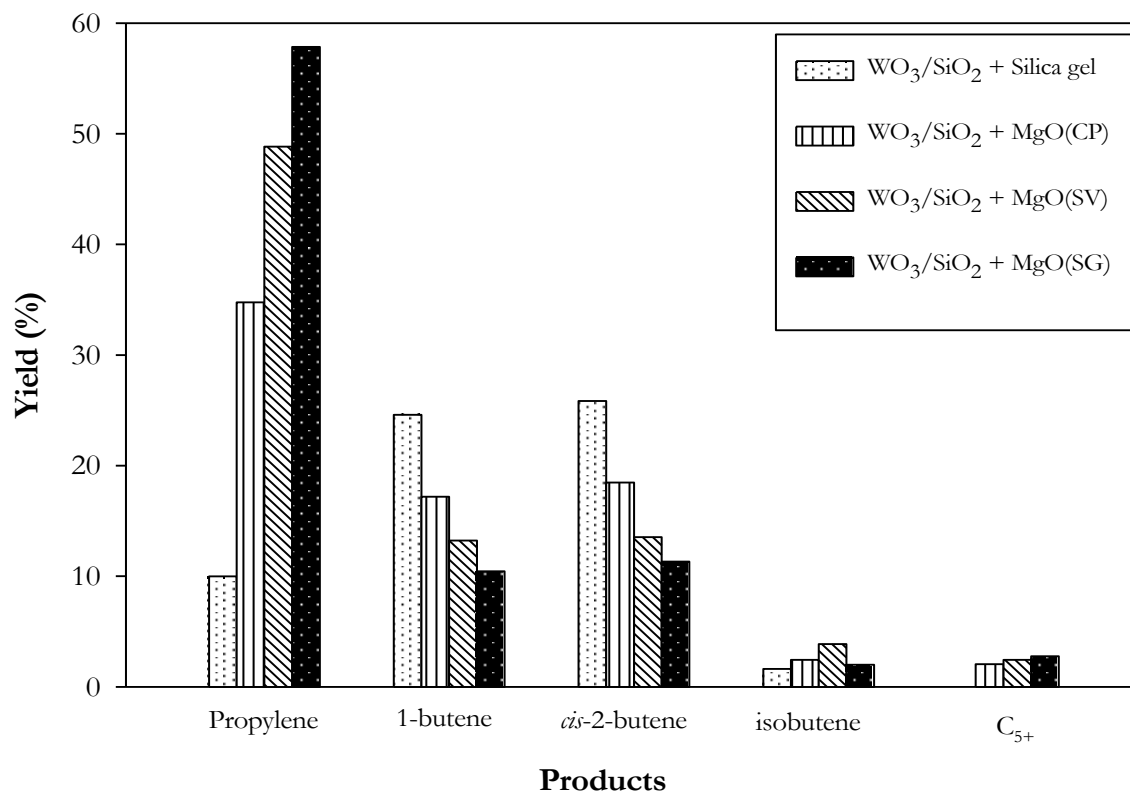| Catalysts	*trans*-2-butene conversion (%)	Selectivity (%)				
		propylene	1-butene	*cis*-2-butene	isobutene	C_{5+}
WO_3/SiO_2 + Silica gel	62.0	16.1	39.6	41.7	2.6	-
WO_3/SiO_2 + MgO(CP)	74.9	46.4	22.9	24.7	3.3	2.7
WO_3/SiO_2 + MgO(SV)	81.9	59.6	16.2	16.5	4.7	3.0
WO_3/SiO_2 + MgO(SG)	84.4	68.5	12.4	13.4	2.4	3.3

Fig. 9.   Product distribution (%yield) after 5 h reaction time of the mixed WO_3/SiO_2 + MgO (or silica gel) catalysts in the cross metathesis of ethylene and *trans*-2-butene.

4. Conclusions

The metathesis of ethylene and *trans*-2-butene was investigated over the physical mixed WO_3/SiO_2 and MgO (1:1 weight ratio) at 450°C in a single catalyst bed. Compared to the WO_3/SiO_2 + silica gel, the use of MgO admixed WO_3/SiO_2 showed much higher 2-butene conversion and propylene selectivity. The major role of the MgO co-catalysts was to convert 1-butene and *cis*-2-butene by-products to *trans*-2-butene, which could further react with excess ethylene, resulting in higher propylene being produced. However, it was noticed that the MgO catalysts containing weak OH adsorption sites showed better performances during the metathesis reaction. Much higher propylene yield can be obtained over the mixed WO_3/SiO_2 + MgO (SG) catalysts than WO_3/SiO_2 + MgO (SV) or WO_3/SiO_2 + MgO (CP). The preparation method used may affect the formation of different OH adsorption sites on MgO (i.e., steps, kinks, divacancies, corners).

Acknowledgments

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