Tungsten Oxide-Modified SSZ-13 Zeolite as an Efficient Catalyst for Ethylene-To-Propylene Reaction

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Abstract: Among the zeolitic catalysts for the ethylene-to-propylene (ETP) reaction, the SSZ-13 zeolite shows the highest catalytic activity based on both its suitable pore architecture and tunable acidity. In this study, in order to improve the propylene selectivity further, the surface of the SSZ-13 zeolite was modified with various amounts of tungsten oxide ranging from 1 wt% to 15 wt% via a simple incipient wetness impregnation method. The prepared catalysts were characterized with several analysis techniques, specifically, powder X-ray diffraction (PXRD), Raman spectroscopy, temperature-programmed reduction of hydrogen (H₂-TPR), temperature-programmed desorption of ammonia (NH₃-TPD), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and N₂ sorption, and their catalytic activities were investigated in a fixed-bed reactor system. The tungsten oxide-modified SSZ-13 catalysts demonstrated significantly improved propylene selectivity and yield compared to the parent H-SSZ-13 catalyst. For the tungsten oxide loading, 10 wt% loading showed the highest propylene yield of 64.9 wt%, which was 6.5 wt% higher than the pristine H-SSZ-13 catalyst. This can be related to not only the milder and decreased strong acid sites but also the diffusion restriction of bulky byproducts, as supported by scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) observation.

Keywords: ethylene-to-propylene; olefin interconversion; SSZ-13; tungsten oxide modification

1. Introduction

The light olefins (C₂–C₄) are essential products of the petrochemical industry and are currently being produced mainly by steam naphtha cracking and fluid catalytic cracking. However, the production of propylene in these processes is not sufficient to meet the increasing global demand [1]. To fill the gap between propylene supply and increasing demand, on-purpose production technologies of propylene (propane dehydrogenation, catalytic cracking of C₄ alkenes, methanol-to-propylene, olefin metathesis, ethylene-to-propylene, etc.) have been proposed as alternatives to the industrial processes [2–6]. Recently, among these technologies, the direct conversion of ethylene-to-propylene (ETP) has received broad attention, and is desired for producing propylene at a high yield from ethylene alone as a starting material in connection with ethane cracker using a low-cost natural gas [7].

Several types of zeolitic materials such as ZSM-5 [7,8], SAPO-34 [5,9,10], UZM-35 [11], and SSZ-13 [2,12–17] have been well documented as possible ETP catalysts to date. In particular, the SSZ-13 zeolite with a chabazite (CHA) topology has exhibited higher propylene selectivity compared to others. It was reported that the high selectivity of propylene directly correlated to the acidity of the SSZ-13 zeolite [5,8,13]. Dai et al. studied the correlation between ETP reactivity and the acidity of the SSZ-13 zeolite by dealuminating the H-SSZ-13 zeolite [2]. More recently, Jun et al. synthesized a series of SSZ-13 zeolites with different
silica/alumina ratios to find the optimum acidity for the ETP reaction [15]. However, the direct ETP reaction over microporous zeolites still suffers from the formation of undesired products such as 1-butene (1-C_4H_8), 2-butenes (i-2-C_4H_8 and c-2-C_4H_8), isobutene (i-C_4H_8), and C_5+ hydrocarbons.

The supported tungsten oxide catalysts have been widely studied due to their excellent performance in producing propylene by the olefin metathesis reaction [18,19]. Considering the tungsten oxide effect, it is anticipated that additional propylene formation will be possible over the reaction between 2-butenes as side products and unreacted ethylene by loading tungsten oxide on the SSZ-13 zeolite in the ETP reaction. In this study, for the first time, we explored the possibility of enhancing the propylene yield by suppressing the undesired products over the tungsten oxide-modified SSZ-13 (WO_3-SSZ-13) catalyst during the ETP reaction.

2. Results and Discussion

Figure 1a shows the PXRD patterns of the H-SSZ-13 and WO_3-SSZ-13 zeolites with different loading amounts of tungsten oxide (1, 5, 10, and 15 wt%). All samples have the main characteristic peaks of the CHA structure. Additionally, new peaks at the 2θ of 23.1, 23.6, 24.3, 33.3, and 34.1 appeared as the loading amount was increased from 5 wt%. The peaks are assigned to the crystalline phase of WO_3. The growth of correspondent WO_3 peaks implies the formation of larger aggregated and isolated WO_3 particles [20]. Whereas at the low WO_3 loading amount (1 wt%) in the SSZ-13 zeolite, the distinct XRD peaks for WO_3 were not observed due to the formation of the amorphous phase of WO_x species or a small amount of WO_3.

![Figure 1. (a) PXRD patterns, (b) Raman spectra, (c) H₂-TPR profiles, and (d) NH₃-TPD profiles of the H-SSZ-13 and WO₃-SSZ-13 samples.](image-url)
To obtain further information on the WO$_3$ particles in the SSZ-13 crystal, Raman spectra and H$_2$-TPR profiles of all samples were collected and the results are shown in Figure 1b,c, respectively. The Raman spectra depict that the aggregated WO$_3$ species, including the amorphous and crystalline phase, continuously increase with an increase of the WO$_3$ loading from the 5 wt% WO$_3$-SSZ-13 sample, as reflected by stronger bands at 276, 716, and 807 cm$^{-1}$. These bands were respectively assigned to the deformation vibration mode of W–O–W, the bending vibration mode of W–O, and the symmetric stretching vibration mode of W–O. The broad band at 964 cm$^{-1}$ was assigned to the symmetric stretching vibration mode of O=W=O of isolated surface tetrahedral WO$_3$ species [21]. From the H$_2$-TPR analysis, a peak corresponding to the reduction of WO$_3$ species appeared at 640 °C in the 5 wt% loaded sample. The peak intensity became higher and the center of the peak shifted to a higher temperature as the WO$_3$ loading increased. Both the Raman and H$_2$-TPR analyses confirmed that the aggregation of WO$_3$ started after 5 wt% loading.

The acidic properties of all samples were analyzed by NH$_3$-TPD measurement and the results are shown in Figure 1d and Table 1. The weak acid site number grew with an increase of WO$_3$ loading amount and then decreased with further WO$_3$ loading after peaking at 10 wt% loading. On the other hand, the strong acid site number decreased until 5 wt% WO$_3$ loading and increased slightly with further loading. It is important to note that all WO$_3$-modified samples showed a lower number of strong acid sites and this may be due to blockage and deactivation of Brønsted acid sites by the formation of WO$_3$ aggregation [20]. Table 1 includes the contents of WO$_3$ and textural properties of the WO$_3$-SSZ-13 zeolites obtained from the ICP-AES analysis and nitrogen adsorption measurement. It was found that the WO$_3$-SSZ-13 zeolites have similar amounts of WO$_3$ to their theoretical values. The BET surface area and total pore volume decreased in all WO$_3$-modified samples compared to the mother zeolite due to the filling of interior space of the crystal by WO$_3$ species.

| Samples                        | WO$_3$ (wt%) | S$_{BET}$ (m$^2$ g$^{-1}$) | V$_{total}$ (cm$^3$ g$^{-1}$) | Acid Site Number (mmol g$^{-1}$) |
|--------------------------------|--------------|---------------------------|-------------------------------|---------------------------------|
| H-SSZ-13                       | -            | 813                       | 0.31                          | 0.198                           |
| 1 wt% WO$_3$-SSZ-13            | 0.90         | 787                       | 0.29                          | 0.201                           |
| 5 wt% WO$_3$-SSZ-13            | 4.50         | 750                       | 0.27                          | 0.365                           |
| 10 wt% WO$_3$-SSZ-13           | 9.04         | 725                       | 0.26                          | 0.387                           |
| 15 wt% WO$_3$-SSZ-13           | 13.6         | 692                       | 0.25                          | 0.334                           |

The ETP catalytic reaction results are presented in Figure 2. As shown in Figure 2a, the ethylene conversion dropped with increasing time-on-stream. After loading WO$_3$ on the SSZ-13 zeolite, the decrease of ethylene conversion was dramatically faster with more WO$_3$ loading up to 5 wt%, and then the conversion showed a very gentle downward trend with further 10 wt% and 15 wt% loading. From the thermogravimetric analysis (TGA) and the gas chromatography-mass spectrometry (GC-MS) analysis of coke extracts for the spent samples with different reaction times (data are not shown), the deactivation of the WO$_3$-SSZ-13 catalyst was due to the blockage of the zeolite pores and acid sites by the formation of large coke species [2]. In a reverse manner, the propylene selectivity showed the opposite tendency to the conversion trend (Figure 2b). All WO$_3$-modified samples showed considerably higher propylene selectivity compared to the parent H-SSZ-13 catalyst. The time-on-stream where the propylene starts forming after the induction period (1.5 h in the case of H-SSZ-13) was shortened with loading WO$_3$. From this observation, it is anticipated that the role of tungsten might be attributable to the diffusion restriction of hydrocarbons inside the cages of crystals, which takes place in the induction period according to the ETP reaction mechanism [2]. The highest value of maximum propylene yield (64.9 wt%) was obtained by the 10 wt% WO$_3$-SSZ-13 sample (Figure 2c). The 15 wt% WO$_3$-SSZ-13 sample showed excellent performance with regard to propylene selectivity,
but due to the comparatively reduced conversion, it showed lower propylene yield than the 10 wt% WO$_3$-SSZ-13 sample. Increased propylene yield with time-on-stream occurred with WO$_3$ loading can be ascribed to the decreased strong acid sites. As seen in Figure 2d, the 10 wt% WO$_3$-SSZ-13 exhibited the highest ethylene selectivity at the same ethylene conversion among all samples. Therefore, it is concluded that an optimum loading amount of WO$_3$ was 10 wt% for the highly selective ETP reaction. Figure 3 shows the correlation between WO$_3$ loading and ETP reactivity in terms of propylene yield and selectivity. It is noteworthy that even a small amount of WO$_3$ loading (1 wt%) led to a noticeable change in propylene selectivity and yield.

Figure 2. Results of ETP reaction over H-SSZ-13 and WO$_3$-SSZ-13 samples. (a) Ethylene conversion, (b) propylene selectivity, and (c) propylene yield as a function of time on stream; (d) propylene selectivity against ethylene conversion.

The product selectivity at ca. 65 wt% of ethylene conversion for all samples is shown in Figure 3. As illustrated in Figure 4 and listed in Table 2, significant changes in product selectivity were observed in C$_3$H$_6$, i-C$_4$H$_8$, and C$_5+$ hydrocarbons, whereas other products remained nearly the same.

The unchanged selectivity of 2-butenes (t-2-C$_4$H$_8$ and c-2-C$_4$H$_8$) may suggest that the effect of WO$_3$ is not due to the olefin metathesis because the reaction conditions for the olefin metathesis and ETP are not the same (the olefin metathesis reaction is generally performed under conditions of 350 °C–450 °C and 20 bar–25 bar) [22]. Instead, there are two possible explanations: (i) the strength and number of the strong acid sites respectively became milder and decreased with further WO$_3$ loading, leading to higher propylene selectivity. Interestingly, a decrease in selectivity of only bulky side products such as i-C$_4$H$_8$ and C$_5+$ species rather than other products suggests that there is another possibility (ii) of a WO$_3$ effect that takes place in sieving intermediates during the ETP reaction according to their kinetic diameters.

Figure 3. The relationship between WO$_3$ loading and ETP reactivity.
selectivity were observed in C3H6, i-C4H8, and C5+ hydrocarbons, whereas other products remained nearly the same.

Figure 4. Product selectivity at ca. 65 wt% ethylene conversion for the H-SSZ-13 and WO3-SSZ-13 samples.

Table 2. Product selectivity and carbon balance at ca. 65 wt% ethylene conversion for the H-SSZ-13 and WO3-SSZ-13 samples.

| Sample       | CH4 | C2H6 | C3H8  | C3H6 | i-C4H10 | n-C4H10 | t-C4H8 | t-2-C4H8 | i-C5H8 | c-2-C4H8 | C5+ | Carbon Balance (%) |
|--------------|-----|------|-------|------|---------|---------|--------|----------|--------|----------|-----|-------------------|
| H-SSZ-13     | 0.43| 3.27 | 2.58  | 75.83| 0.27    | 0.25    | 0.98   | 2.33     | 2.38   | 1.47     | 10.19| 98.9              |
| 1 wt% WO3-SSZ-13 | 0.40| 3.28 | 3.13  | 82.62| 0.05    | 0.26    | 0.75   | 1.80     | 0.88   | 1.10     | 6.7  | 99.2              |
| 5 wt% WO3-SSZ-13 | 0.42| 3.36 | 4.02  | 86.04| 0      | 0.42    | 0.71   | 1.77     | 0.17   | 1.01     | 2.05 | 98.3              |
| 10 wt% WO3-SSZ-13| 0.39| 3.16 | 3.50  | 85.84| 0.07    | 0.42    | 0.82   | 2.07     | 0.19   | 1.20     | 2.30 | 98.6              |
| 15 wt% WO3-SSZ-13| 0.41| 3.35 | 3.73  | 85.55| 0      | 0.34    | 0.77   | 1.96     | 0.23   | 1.12     | 2.53 | 98.4              |

The unchanged selectivity of 2-butenes (t-2-C4H8 and c-2-C4H8) may suggest that the effect of WO3 is not due to the olefin metathesis because the reaction conditions for the olefin metathesis and ETP are not the same (the olefin metathesis reaction is generally performed under conditions of 350 °C–450 °C and 20 bar–25 bar) [22]. Instead, there are two possible explanations: (i) the strength and number of the strong acid sites respectively became milder and decreased with further WO3 loading, leading to higher propylene selectivity. Interestingly, a decrease in selectivity of only bulky side products such as i-C4H8 and C5+ species rather than other products suggests that there is another possibility (ii) of a WO3 effect that takes place in sieving intermediates during the ETP reaction according to their kinetic diameters.

In order to clarify the latter sieving effect in crystals of SSZ-13 after modification, STEM and EDS images are presented in Figure 5a,b with 1 wt% WO3-SSZ-13 and 10 wt% WO3-SSZ-13 samples, respectively. It can be seen that the WO3 species was not evenly distributed throughout the crystals. Both line scanning and EDS measurements confirm that the intensity corresponding to the outer part of the crystals was more severe than that of the inner part of the crystals. This means that WO3 species are dominantly deposited at the outer part of the crystals, which could be an indication of partial blockage of the pore window.
Table 2. Product selectivity and carbon balance at ca. 65 wt% ethylene conversion for the H-SSZ-13 and WO3-SSZ-13 samples.

| Sample          | Selectivity (wt%) | Carbon Balance (%) |
|-----------------|-------------------|--------------------|
|                 | CH4               | C2H6               | C3H8 | C3H6 | i-C4H10 | n-C4H10 | 1-C4H8 | t-C4H8 | i-C4H8 | C5+ |
| H-SSZ-13        | 0.43              | 3.27               | 2.58 | 75.83| 0.27    | 0.25    | 0.98   | 2.33   | 2.38   | 1.47 |
| 1 wt% WO3-SSZ-13| 0.40              | 3.28               | 3.13 | 82.62| 0.05    | 0.26    | 0.75   | 1.80   | 0.88   | 1.10 |
| 5 wt% WO3-SSZ-13| 0.42              | 3.36               | 4.02 | 86.04| 0.00    | 0.42    | 0.71   | 1.77   | 0.17   | 1.01 |
| 10 wt% WO3-SSZ-13| 0.39             | 3.16               | 3.50 | 85.84| 0.07    | 0.34    | 0.82   | 2.07   | 0.19   | 1.20 |
| 15 wt% WO3-SSZ-13| 0.41             | 3.35               | 3.73 | 85.55| 0.00    | 0.34    | 0.77   | 1.96   | 0.23   | 1.12 |

In order to clarify the latter sieving effect in crystals of SSZ-13 after modification, STEM and EDS images are presented in Figure 5a,b with 1 wt% WO3-SSZ-13 and 10 wt% WO3-SSZ-13 samples, respectively. It can be seen that the WO3 species was not evenly distributed throughout the crystals. Both line scanning and EDS measurements confirm that the intensity corresponding to the outer part of the crystals was more severe than that of the inner part of the crystals. This means that WO3 species are dominantly deposited at the outer part of the crystals, which could be an indication of partial blockage of the pore window.

Therefore, it is expected that the tungsten-modified samples will have a smaller pore window size compared to pristine H-SSZ-13 (the size of the pore window in SSZ-13 is 3.8 Å). Due to reduction in the size of pore window caused by WO3 modification, only bulky intermediates such as isobutene and C5+ having higher kinetic diameters (di-C4H8 = 4.84 Å, di-C4H8 < dC5+ respectively) compared to others (n-butane (4.687 Å), 1-butene (4.46 Å) and trans-2-butene (4.31 Å)) face additional diffusion hindrance inside the cages of crystals while escaping from the cages during the ETP reaction [23]. These bulky compounds that fail to escape could readily be converted to alkyl-naphthalene intermediates, which enables increased propylene selectivity via the alkyl-naphthalene-based mechanism in the ETP reaction [2]. Thus, the propylene yield overall increased selectively.

3. Materials and Methods
3.1. Catalysts Preparation

The SSZ-13 zeolite was synthesized according to the interzeolite conversion method using Y zeolite published elsewhere [24]. The synthesized zeolite was ion-exchanged using a 1.0 M NH4NO3 solution (10 mL solution per 1.0 g of the zeolite) at 60 °C for 6 h, followed by calcination at 600 °C for 6 h. The exchange-calcination process was repeated three times and the resultant sample is denoted as “H-SSZ-13”. The WO3-SSZ-13 zeolites were prepared via an incipient wetness impregnation method with varied amounts of WO3 precursor. A mixture of 0.3 mL of distilled water and the calculated amount of phosphotungstic acid hydrate (H3[P(W3O10)4]·xH2O, Sigma-Aldrich, St. Louis, MO, USA) was slowly added to 1.0 g of H-SSZ-13 powder, followed by rigorous mixing using a spatula. The solid was dried at 100 °C and calcined at 600 °C for 6 h.
3.2. Catalysts Characterization

The PXRD patterns were collected by a Rigaku Miniplex diffractometer using a monochromatized X-ray beam from Cu-Kα radiation (λ = 1.54056 nm) at 30 kV and 15 mA. Raman spectra were recorded on a Renishaw Micro Raman Spectrometer in a range from 200 to 1200 cm\(^{-1}\) (excitation line: 785 nm of diode solid-state laser). H\(_2\)-TPR profiles were taken using a Micromeritics AutoChem II 2920 instrument. NH\(_3\)-TPD profiles were obtained using a BEL Japan BELCAT instrument. The amount of weak and strong acid sites were estimated from the amount of NH\(_3\) desorbed from 100 °C to 300 °C and from 300 °C to 650 °C, respectively. The WO\(_3\) content in the samples was analyzed by ICP-AES using a Spectro Ciros Vision instrument. A nitrogen adsorption analysis was performed at −196 °C using a Micromeritics Tristar 3000 volumetric gas adsorption analyzer. STEM images and EDS elemental mapping images were collected using a Titan cubed G2 60–300 microscope with a spherical aberration corrector operated at 300 kV.

3.3. Catalytic Test

The ETP reaction was carried out in a 1/2 inch fixed-bed reactor using 0.5 g of the catalyst. The catalyst was pre-treated at 500 °C for 2 h under a helium flow at a rate of 50 mL min\(^{-1}\). The catalytic reaction was performed at 330 °C and 0.33 h\(^{-1}\) of WHSV under ambient pressure. The ethylene and nitrogen inlet flow were kept at a rate of 2.2 and 5.2 mL min\(^{-1}\), respectively. The effluent products were analyzed by an online gas chromatograph (YL6500 GC, Young In Chromass, Anyang, Korea) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). Conversion of ethylene and selectivity and yield of propylene were evaluated as follows:

\[
\text{Conversion of ethylene (wt\%)} = \frac{\text{mass of reacted ethylene}}{\text{mass of fed ethylene}} \times 100 \quad (1)
\]

\[
\text{Selectivity of product (wt\%)} = \frac{\text{mass of formed product}}{\text{mass of reacted ethylene}} \times 100 \quad (2)
\]

\[
\text{Yield of propylene (wt\%)} = \frac{\text{Conversion of ethylene} \times \text{Selectivity of propylene}}{100} \quad (3)
\]

4. Conclusions

Considering the olefin metathesis effect, the H-SSZ-13 zeolite was modified with tungsten oxide for the ETP reaction in order to improve the propylene selectivity. WO\(_3\) was introduced via a simple incipient wetness impregnation method and the amount of WO\(_3\) was varied from 1 wt\% to 15 wt\%. The results of the ETP reaction revealed that WO\(_3\) loading on the H-SSZ-13 could enhance the selectivity and yield of propylene considerably compared to the pristine H-SSZ-13 catalyst. The highest selectivity and yield of propylene were obtained by the 10 wt\% WO\(_3\) loading sample. Interestingly, it appears that the role of WO\(_3\) in the ETP reaction is not due to the olefin metathesis reaction because of the unchanged selectivity of 2-butenes (t-2-C\(_4\)H\(_8\) and c-2-C\(_4\)H\(_8\)) from the ETP results. Instead, the increased propylene selectivity after WO\(_3\) loading can be attributed to the reduced Brønsted acidity and the formation of additional diffusion restriction for the bulk byproducts, as supported by STEM-EDS observation.

We have experimentally shown the possibility of increasing propylene yield by suppressing the undesirable products (isobutene and C\(_5\+)\) species) correspondingly on account of the WO\(_3\) effect. To further elucidate the effect of WO\(_3\) on ETP reactivity, detailed research on intracrystalline diffusivity is proposed as future work. The additional diffusion hindrance parameters can be determined through intracrystalline diffusion study, which would be helpful to control propylene selectivity in the ETP reaction by tuning the diffusivity. Moreover, this strategy could be extended to apply heteroatoms or other metal oxide species on the SSZ-13 zeolite for obtaining highly selective ETP catalysts.
Author Contributions: Conceptualization, T.-W.K.; methodology, M.U.u.A. and S.L.; validation, S.L.; formal analysis, M.U.u.A.; investigation, M.U.u.A.; resources, M.U.u.A.; writing—original draft preparation, M.U.u.A.; writing—review and editing, S.L., T.-W.K. and C.-U.K.; visualization, M.U.u.A.; supervision, C.-U.K.; project administration, T.-W.K.; funding acquisition, T.-W.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by project No. 2017M1A2A2047442 supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning.

Data Availability Statement: All relevant data are contained in the present manuscript. Other inherent data are available on request from the corresponding author.

Acknowledgments: This research was supported by the Korea Research Institute of Chemical Technology (KRICT) funded by project No. SI2012-10 (Energy-saving process and technology of chemical production for response to climate change), and project No. 2017M1A2A2047442 supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning.

Conflicts of Interest: The authors declare no conflict of interest.

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