

Article

Performance of Ethane Dehydrogenation over PtSn Loaded onto a Calcined Mg(Al)O LDH with Three Mg:Al Molar Ratios Using a Novel Method

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Abstract: Layered double hydroxide (LDH) is a layered solid containing positively charged layers with negatively charged anions as an interchangeable interlayer. In this research, Mg(Al)O supports were synthesized with three different Mg:Al molar ratios, and bimetallic PtSn catalysts were loaded onto the supports via the anion exchange method. The properties of ethane dehydrogenation of the PtSn/Mg(Al)O catalysts were investigated. The results show that the structure and properties of the PtSn/Mg(Al)O catalysts were influenced by the Mg:Al molar ratio of the hydrotalcites, which consequently influenced the ethane dehydrogenation performance. When the Mg:Al ratio was 5:1, the ethane dehydrogenation performance was optimal, relative to the Mg:Al ratios of 2:1 and 10:1.

Keywords: hydrotalcite; Mg:Al molar ratio; anion exchange method; ethane dehydrogenation

1. Introduction

The production of light alkenes is an indicator of the developmental degree of the national petrochemical industry [1,2]. Traditionally, light alkenes are produced through petroleum cracking. However, a shortage of oil resources and refining capacity severely limit the supply of light alkenes. Therefore, it is urgent to develop other means of producing light alkenes [3,4]. With the rapid development of shell gas and natural gas, the catalytic dehydrogenation of light alkanes can be a more economical and environmentally friendly method of production when compared with traditional methods [1–4].

Platinum is widely studied for its use in the dehydrogenation of light alkanes. However, when only Pt is loaded onto the supports, there exists low olefin selectivity, and the rapid deactivation of catalysts occurs [5–9]. It was found that the addition of Sn can suppress the coking reaction, as well as decrease the sintering of the metal, further inhibiting the deactivation of catalysts [10–13].

The catalytic behavior of the alkane dehydrogenation reaction is very dependent on the method of PtSn preparation [14–16]. For example, Vertes et al. compared the alkane dehydrogenation performances of PtSn/ γ -Al₂O₃ catalysts prepared via two different methods. They found that different catalysts synthesized via two different methods had different states of tin (one was the ionic state, and the other was the superficial PtSn_x alloy state). Furthermore, different alkane dehydrogenation performances were observed [15]. Baronetti et al. found that co-impregnation or successive impregnation can also influence the final properties of PtSn [16]. Preparation techniques

play a significant role in controlling interactions that occur between tin and platinum, as well as those between these metals and the support, thus influencing catalytic performance [14,17].

The support is also crucial for ethane dehydrogenation. Good supports must be thermally stable and possess an appropriate level of acidity, a large surface area, and uniform pore-size distribution for the effective dehydrogenation of alkanes [2]. Recent studies showed that the calcined layered double hydroxide is a great support for the light alkane dehydrogenation reaction. Mg(Al)O is an especially attractive support because it is moderately basic and exhibits high thermal stability. Moreover, the Al cations at the support surface help stabilize the dispersed metal particles against sintering [18–21].

A layered double hydroxide (LDH) is a layered solid containing positively charged layers and an exchangeable interlayered negative charge. The main structure of hydrotalcite is formed by a positively charged layer and an anion interlayer. The interlayered anions may be inorganic anions, organic anions, or heteropoly anions, and these interlayered anions have exchangeability properties [22,23]. Therefore, the exchangeability of hydrotalcites can be used for the synthesis of catalysts via the anion exchange method [24]. However, few papers report on the use of a PtSn/LDH catalyst synthesized via anion exchange for light alkane dehydrogenation. In a study by Bell et al., Pt, PtIr, and PtSn nanoparticles were synthesized in organic solvents and dispersed in toluene, before being added to a suspension of Mg(Al)O in anhydrous toluene. The mixture was stirred overnight, and the resulting product was precipitated by tripling the volume with the addition of anhydrous ethanol, before being separated by centrifugation. The solid material was heated at 723 K for 1 h in air to remove the surface capping agents, and was then reduced in an atmosphere of H₂ in Ar [13]. The other method involved the introduction of Pt onto calcined Mg(Al)O via the incipient wetness impregnation of Pt(acetylacetonate)₂ dissolved in toluene [18]. In Virnovskaia's work, active metals in the high-loading catalysts, Pt/Mg(Al)O, Sn/Mg(Al)O, and PtSn/Mg(Al)O, were also deposited onto uncalcined hydrotalcite via the impregnation method [21]. In our previous work, we used the anion exchange method to load the PtSn metals; however, that work aimed to determine the promotion effect of Ga for ethane dehydrogenation [20]. Thus, the synthesis of a PtSn metal via the anion exchange method using the properties of LDHs is a novel method for alkane dehydrogenation.

In this study, Mg(Al)O LDHs were synthesized as supports with three different Mg:Al molar ratios, and the PtSn metal particles were prepared via the anion exchange method. The influences of loading PtSn via the anion exchange method were investigated, as was the effect of various Mg:Al molar ratios in the hydrotalcite supports on the performance of ethane dehydrogenation.

2. Results and Discussion

2.1. Synthesis of Mg(Al)O LDH with Different Mg:Al Ratios

The X-ray diffraction (XRD) patterns of Mg(Al)O LDH with different Mg:Al molar ratios are shown in Figure 1. In all cases, characteristic diffraction peaks of magnesium aluminum hydrotalcite materials were detected. Major peaks were detected for (003) at 11.7°, (006) at 23.6°, (110) at 60.9°, and (113) at 62.3° (JSPDS No. 035-0964). The intensity of the XRD increased with an increase in the Mg:Al molar ratio. This indicates that the structure of the Mg(Al)O LDHs improved with higher Mg:Al molar ratios. The XRD characterization also showed that the variation in the Mg:Al molar ratio influenced the crystal structure of the hydrotalcite carrier space. The basal spacing of (003) was calculated to be approximately 0.76 nm, 0.79 nm, and 0.91 nm when the Mg:Al molar ratios were 2:1, 5:1, and 10:1, respectively. This is due to the Al³⁺ ionic radius being smaller than the Mg²⁺ ionic radius; thus, an increase in the Mg:Al molar ratio results in an increase in the average distance of the crystal cell parameters with respect to the adjacent cation, and the charge density of the layer plane decreases, resulting in a reduction in both the subject layer plane and the electrostatic force of interlayer anions, subsequently increasing the spacing.

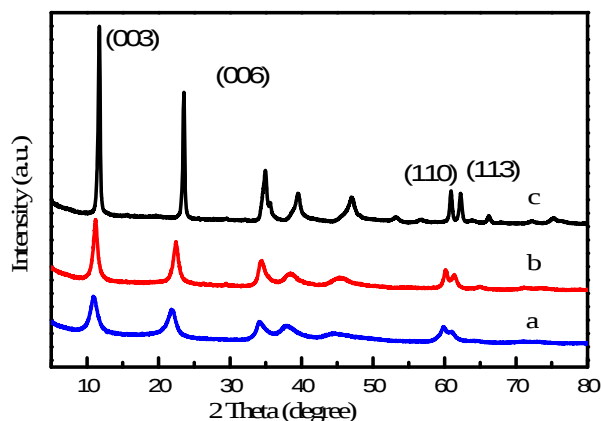


Figure 1. X-ray diffraction (XRD) patterns of Mg(Al)O layered double hydroxides (LDHs) with different Mg:Al molar ratios: (a) Mg:Al = 2:1; (b) Mg:Al = 5:1; (c) Mg:Al = 10:1.

Figure 2 shows TEM images of the Mg(Al)O LDHs with the three different Mg:Al molar ratios. All the TEM images show characteristics typical of magnesium aluminum hydrotalcite. The images reveal that when the Mg:Al ratio was 2:1, small pieces with a size of about 100 nm appeared (Figure 2a,b). When the Mg:Al ratio increased to 5:1, the small pieces became bigger and thinner (Figure 2c,d). When the Mg:Al ratio increased to 10:1, the pieces became much larger, appearing almost bulk in structure (Figure 2e,f). The TEM images are consistent with the XRD results.

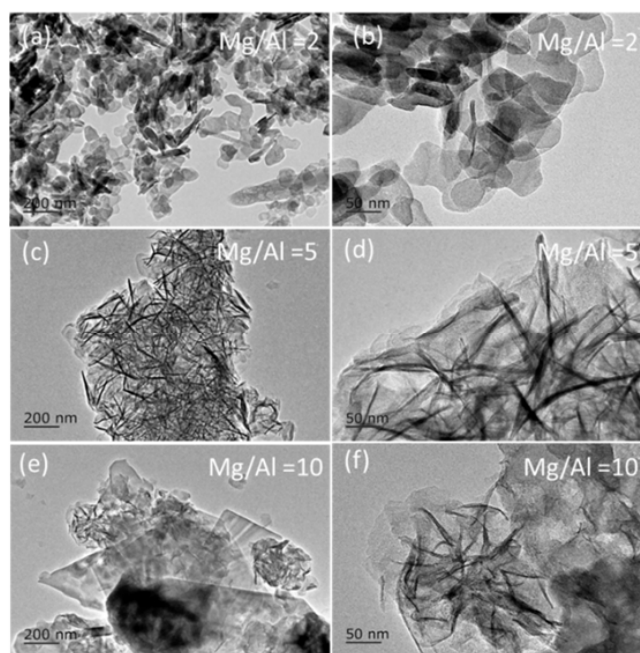


Figure 2. TEM images of Mg(Al)O LDHs with different Mg:Al molar ratios: (a,b) Mg:Al = 2:1; (c,d) Mg:Al = 5:1; (e,f) Mg:Al = 10:1.

2.2. Synthesis of PtSn/Mg(Al)O via the Anion Exchange Method

Figure 3 shows the schematic illustration of loading Pt and Sn precursors onto Mg(Al)O LDHs through the anion exchange method. Hydrotalcite-like layered double hydroxides are a host–guest material consisting of positively charged metal-hydroxide sheets with intercalated anions and water molecules [25–27]. Anions are capable of being intercalated into the interlayers of LDH [28–30]. Therefore, we chose PtCl_6^{2-} and SnO_3^{2-} as precursors for intercalation into the LDHs. PtCl_6^{2-}

and SnO_3^{2-} were loaded onto the LDH through simple anion exchange at 70 °C for 24 h to obtain LDH-Pt(IV)-Sn(IV). The solution was dried at 100 °C overnight, before being reduced in an H_2/N_2 atmosphere at 600 °C. The calcined products of LDHs are often very reactive mixed oxides, called layered double oxides (LDOs). When Pt and Sn were loaded onto Mg(Al)O LDHs through the anion exchange method after calcination, the compound was named PtSn/Mg(Al)O; the catalysts are named PtSn/Mg(Al)O-2, PtSn/Mg(Al)O-5, and PtSn/Mg(Al)O-10 when the Mg:Al ratios were 2:1, 5:1, and 10:1, respectively.

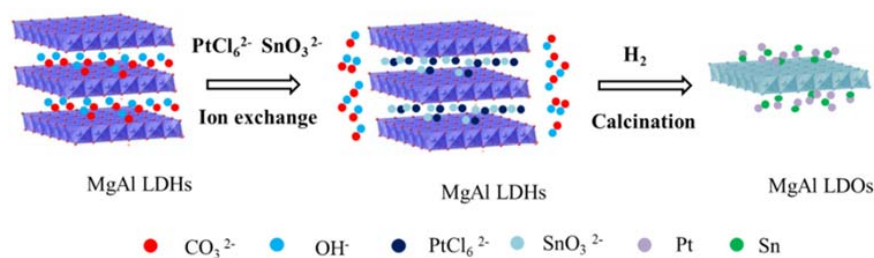


Figure 3. Schematic illustration of loading Pt and Sn precursors onto Mg(Al)O LDHs through the anion exchange method.

Images of the PtSn/Mg(Al)O catalysts with different Mg:Al ratios were captured by TEM (Figure 4). All the images show that the calcined hydrotalcites and the metal particles were dispersed uniformly on the surface of the support. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the corresponding particle-size distributions of PtSn/Mg(Al)O with different Mg:Al ratios are shown in Figure 5. HAADF-STEM images provide further evidence of the average distribution and small PtSn particles on the supports. The mean diameters of the dispersed PtSn particles were 1.50 ± 0.3 nm, 2.26 ± 0.4 nm, and 2.57 ± 0.4 nm when the Mg:Al ratios were 2:1, 5:1, and 10:1, respectively (Figure 5). The results indicate that the particle sizes were less than 3 nm for all tested ratios, and a lower proportion of added Mg resulted in a better metallic particle size in this range.

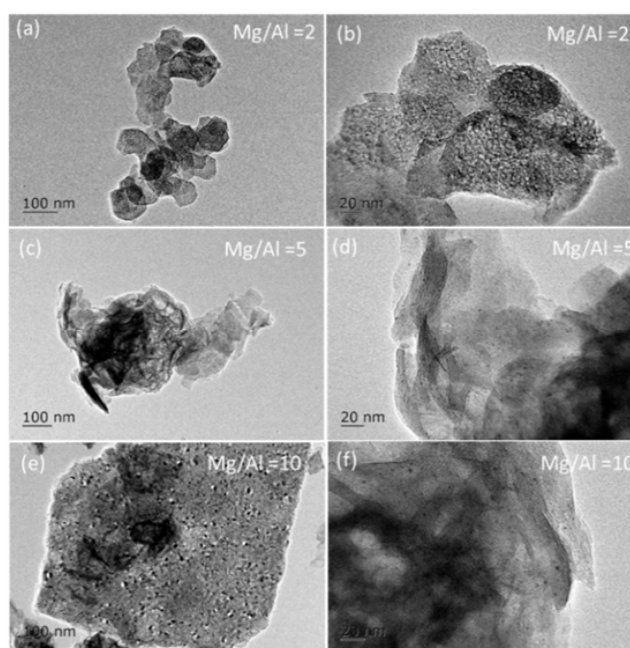


Figure 4. TEM images of PtSn/Mg(Al)O: (a,b) Mg:Al = 2:1; (c,d) Mg:Al = 5:1; (e,f) Mg:Al = 10:1.

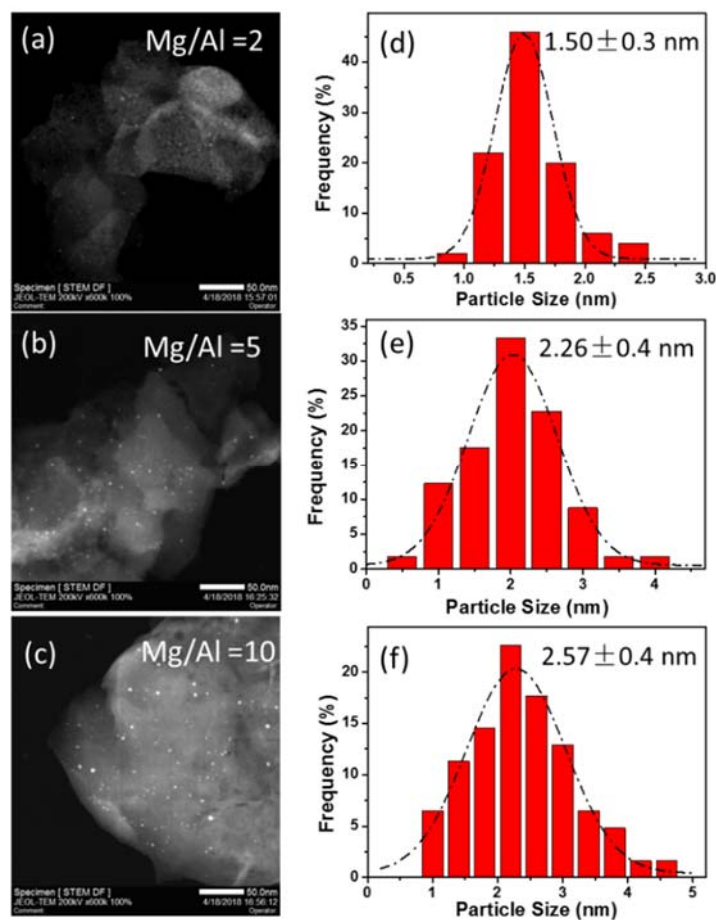


Figure 5. (a–c) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and (d–f) size distribution of metal PtSn/Mg(Al)O particles with different Mg:Al ratios.

The actual percentages of the Pt and Sn to be ion-exchanged into the LDH for each sample were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses. The actual amounts of Pt exchanged onto Mg(Al)O with different Mg:Al ratios were quite similar, with values of 0.34 wt%, 0.35 wt%, and 0.33 wt% (Table 1). The actual amounts of Sn exchanged into all LDHs were also quite similar, with values of 0.08 wt%, 0.09 wt%, and 0.08 wt% (Table 1).

Table 1. The inductively coupled plasma atomic emission spectrometry (ICP-AES) elemental analysis results revealing the amounts of Pt and Sn to be ion-exchanged into the layered double hydroxide (LDH) layer.

Mg:Al Molar Ratio	Sample Mass (g)	Pt (mg/L)	Percentage of Pt (wt%)	Sn (mg/L)	Percentage of Sn (wt%)
2:1	0.1006	3.426	0.34	0.836	0.08
5:1	0.1083	3.780	0.35	1.074	0.09
10:1	0.1006	3.288	0.33	0.842	0.08

The SEM images of PtSn/Mg(Al)O with different Mg:Al molar ratios are displayed in Figure 6. The SEM images clearly indicate a highly sintered material, which is characteristic of solids consisting of aggregates. With increasing Mg:Al ratio, the particle sizes of the aggregates became increasingly large.

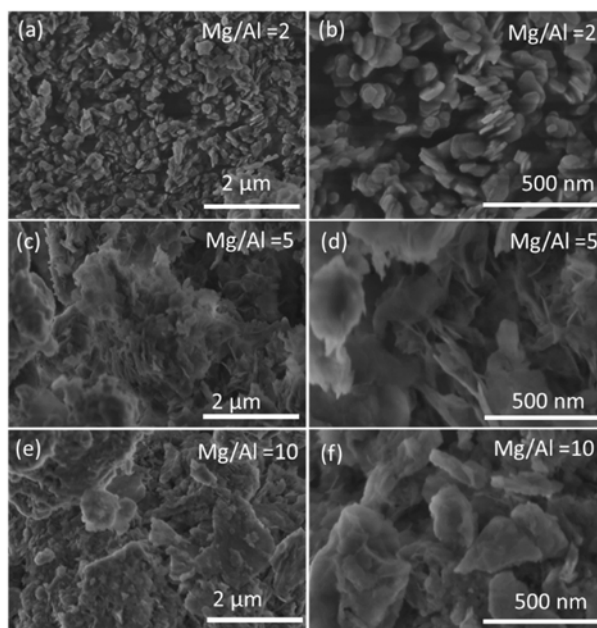


Figure 6. SEM images PtSn/Mg(Al)O with different Mg:Al molar ratios: (a,b) Mg:Al = 2:1; (c,d) Mg:Al = 5:1; (e,f) Mg:Al = 10:1.

2.3. Catalytic Performances of PtSn/Mg(Al)O with Different Mg:Al Ratios in Ethane Dehydrogenation

Figure 7 shows the ethane dehydrogenation reaction performances over PtSn/Mg(Al)O catalysts with different Mg:Al ratios. In Figure 7a, for the sample of PtSn/Mg(Al)O-5, the initial ethane conversion was 18.7%, and the ethane conversion was nearly 20% throughout the 120-min reaction stage. The same phenomenon occurred for PtSn/Mg(Al)O-2. The ethane conversion was consistently almost 18% for the entire stage. For the PtSn/Mg(Al)O-10 sample, the ethane conversion was 18.1% in the initial stage, before decreasing quickly during the first 20 min, and ultimately decreasing to 11.1% after 120 min. The results demonstrate that, when the Mg:Al ratio was 5:1, ethane conversion exhibited the highest catalytic activity.

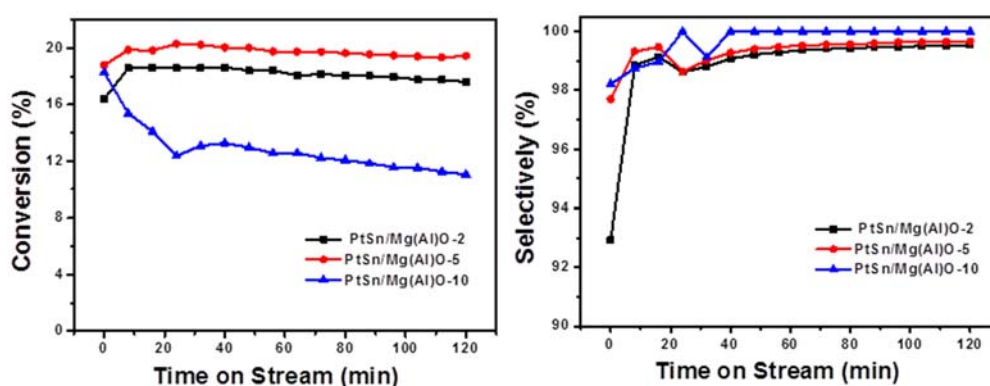


Figure 7. (a) Ethane conversion and (b) ethylene selectivity of PtSn/Mg(Al)O catalysts. Reaction conditions: 550 °C, 50 mg of catalyst, 0.2 bar C₂H₆, 0.8 bar N₂, C₂H₆ weight hourly space velocity (WHSV) of 12.9 h⁻¹.

Ethylene selectivity was strongly related to the Mg:Al ratio. Figure 7b reveals that the PtSn/MgAlO-2 selectivity was 92.9% in the initial stage, before increasing rapidly to 98.8% at 8 min, and then slowly stabilizing for 120 min. For PtSn/MgAlO-5, the selectivity was 97.7% in the initial stage, before increasing rapidly to 99.3% at 8 min, and then slowly stabilizing for 120 min (>99%).

For PtSn/MgAlO-10, the selectivity was 98.2% in the initial stage, before increasing rapidly to 98.7% at 8 min, and then slowly stabilizing for 120 min (>99%).

The selectivity of PtSn/Mg(Al)O-10 was the highest; however, its conversion was the lowest. The conversion of PtSn/Mg(Al)O-2 was intermediate; however, its selectivity was the lowest. The PtSn/Mg(Al)O-5 catalyst had the highest catalytic activity and a relatively high selectivity. Thus, the moderate Mg:Al ratio of the PtSn/Mg(Al)O catalyst is appropriate for the ethane dehydrogenation reaction.

2.4. Discussion of PtSn/Mg(Al)O with Different Mg:Al Ratios in Ethane Dehydrogenation

Figure 8a presents the XRD patterns of Mg(Al)O LDHs loaded with PtSn via the anion exchange method after calcination, resulting in the characteristic structure of periclase (MgO). The diffraction peaks of hydrotalcite disappeared. Previous works showed that the calcination products of magnesium aluminum hydrotalcite have a MgO-like structure, where Al and Ga ions are dissolved in the lattice, forming a solid solution [31]. With an increase in the Mg:Al molar ratio, the intensity of the diffraction peaks increased. Moreover, there is no signal from the Pt or Sn species because of their low concentrations.

Figure 8b shows the formation of the crystalline phase—which occurred during the calcination of Mg(Al)O LDHs—at various temperatures between 50 °C and 650 °C. The calcined products of LDHs are very reactive mixed oxides, called layered double oxides (LDOs) [32]. The in situ XRD patterns show that the whole process was divided into three temperature regions: 50–200 °C, 200–300 °C, and 300–650 °C. For the first region of calcination, from 50–200 °C, the main diffraction peaks were attributed to the structure of LDHs. In this stage, the main process was the removal of physically absorbed water, which did not change the structure of LDHs [32]. For the second region, with temperatures between 250 and 300 °C, the peak at 13°—corresponding to the plane (003) of LDHs—disappeared, and the diffraction peaks were slightly broader; however, the layer structure still existed. As the temperature continued increasing, the diffraction peaks attributed to the LDHs totally disappeared, indicating that the layer structure collapsed completely at this point. When the calcination temperature reached 350 °C, two broad diffraction peaks appeared, which were roughly attributed to a periclase MgO-like mixed oxide structure. As the calcination temperature increased to 650 °C, there was no obvious change in the diffraction peak positions. Meanwhile, the intensity of the diffraction peaks increased. However, this does mean that crystallinity increased with increasing temperature.

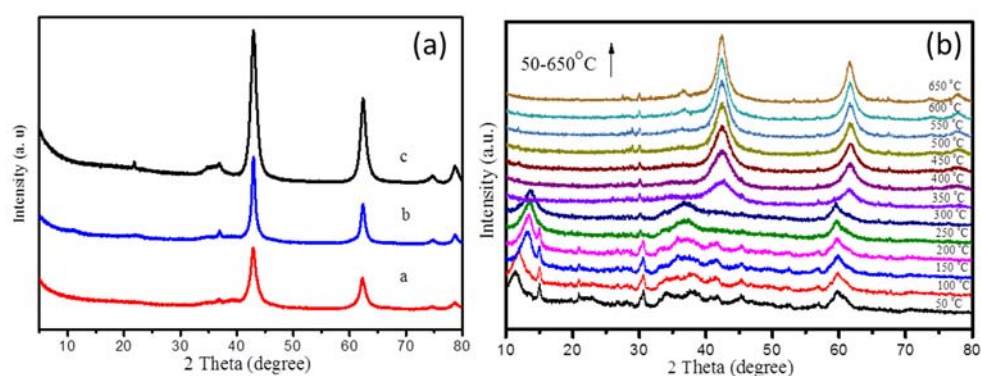


Figure 8. (a) X-ray diffraction patterns of PtSn/Mg(Al)O with different Mg:Al molar ratios: a: Mg:Al = 2:1; b: Mg:Al = 5:1; c: Mg:Al = 10:1. (b) In situ X-ray diffraction patterns of Mg(Al)O (Mg:Al = 5:1) LDH at temperatures between 50 and 650 °C.

To evaluate the textural properties of the series of PtSn/Mg(Al)O catalysts, a low-temperature N₂ adsorption–desorption isotherm experiment was carried out, and the results are shown in Figure 9. All samples revealed typical V-type adsorption isotherms, indicating a typical mesoporous structure.

Table 1 shows the low-temperature N_2 adsorption–desorption data of the catalysts. The S_{BET} values were $188\text{ m}^2/\text{g}$, $113\text{ m}^2/\text{g}$, and $85\text{ m}^2/\text{g}$ when the Mg:Al ratios were 2:1, 5:1, and 10:1, respectively. The results mean that the S_{BET} value is inversely correlated with the Mg:Al ratio. Furthermore, the pore volume has a tendency to be positively correlated with the Mg:Al ratio, with values of $0.30\text{ cm}^3/\text{g}$, $0.65\text{ cm}^3/\text{g}$, and $0.54\text{ cm}^3/\text{g}$, respectively. The results indicate that the structure of PtSn/Mg(Al)O changed to some extent. According to the textural parameters in Table 2, the PtSn/Mg(Al)O-5 sample had a moderate S_{BET} value and the highest pore volume. The surface structure and pore volume have a great influence on the activity and selectivity of alkane dehydrogenation. A relatively large surface area and uniform pore-size distribution can lead to an optimal distribution of the PtSn particle structure, thus resulting in a higher ethane dehydrogenation activity.

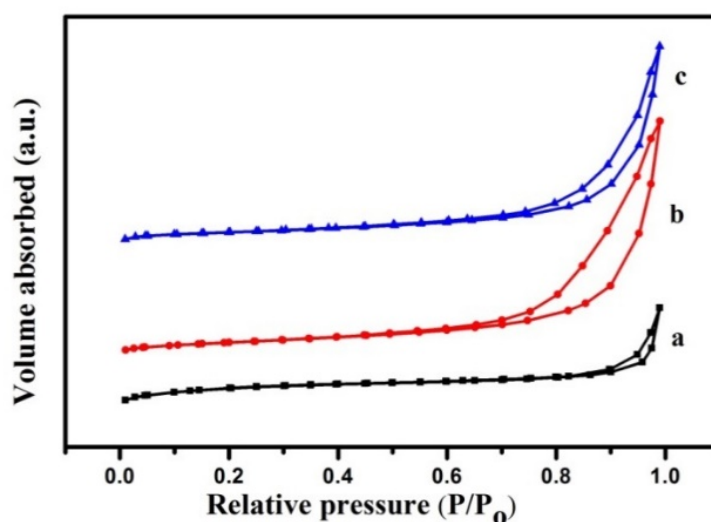


Figure 9. Low-temperature N_2 adsorption–desorption isotherms of PtSn/Mg(Al)O with different Mg:Al ratios: (a) Mg:Al = 2:1; (b) Mg:Al = 5:1; (c) Mg:Al = 10:1.

Table 2. Textural properties of PtSn/Mg(Al)O catalysts with Mg:Al ratios of 2:1 (Mg(Al)O-2), 5:1 (Mg(Al)O-5), and 10:1 (Mg(Al)O-10).

Sample	Mg:Al Molar Ratio	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Mg(Al)O-2	2:1	188.0	0.30
Mg(Al)O-5	5:1	113.0	0.65
Mg(Al)O-10	10:1	84.8	0.54

It is well known that optimal acidity and basicity of the supports are needed to avoid undesirable side reactions. Mg(Al)O is particularly attractive because it has moderate acid–base properties, and it exhibits high thermal stability to steam and reduction–oxidation cycling [2]. Therefore, the ethane dehydrogenation activity is also related to the support’s acidity and basicity [2]. The acidic properties were investigated using the temperature-programmed desorption of NH_3 (NH_3 -TPD) method, and the results are shown in Figure 10. For the PtSn/Mg(Al)O-2 and PtSn/Mg(Al)O-5 samples, the results show three peaks around 217°C , 511°C , and 590°C , attributed to weak, medium, and strong acid sites, respectively [17,33–35]. The pulse results show that total acidity was $1242.2\text{ }\mu\text{mol/g}$ and $945.0\text{ }\mu\text{mol/g}$, respectively. For PtSn/Mg(Al)O-10, the peak ascribed to moderate acid sites disappeared, and the total acidity was $655.0\text{ }\mu\text{mol/g}$. It can be seen that the total acidity of the catalysts decreased with an increase in Mg:Al molar ratio. This is due to the presence of a greater proportion of Al, which creates more acid sites. The increase in the number of acid sites in the catalyst can improve the dehydrogenation performance; however, it can also lead to deep cracking of dehydrogenation products, which facilitates carbon inactivation of the catalysts.

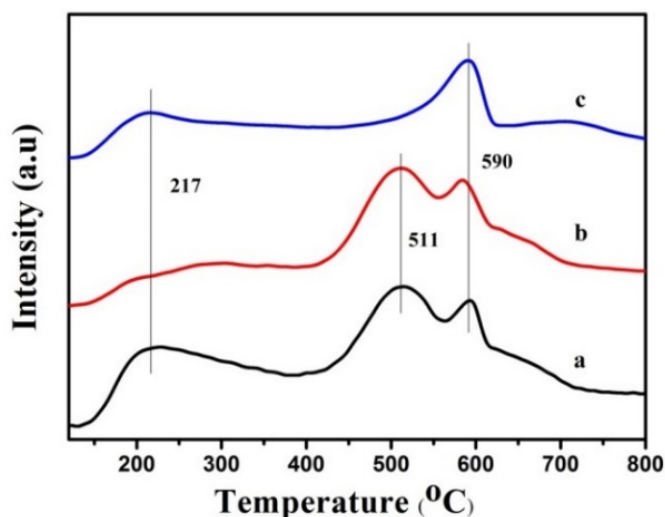


Figure 10. Temperature-programmed desorption of NH_3 (NH_3 -TPD) profiles of PtSn/Mg(Al)O with different Mg:Al ratios: (a) $\text{Mg:Al} = 2:1$; (b) $\text{Mg:Al} = 5:1$; (c) $\text{Mg:Al} = 10:1$.

The temperature-programmed desorption of CO_2 (CO_2 -TPD) was used to detect the surface basicity of the catalyst series. Figure 11 reveals three CO_2 desorption peaks for all samples, two of which were around 200 °C and 290 °C, attributed to weak and moderate basicity sites; the third peak was around 500 °C, and was attributed to strong basicity [33–35]. As the Mg:Al ratio increased, the desorption peaks ascribed to weak and medium basicity shifted to higher temperatures, and the intensity increased.

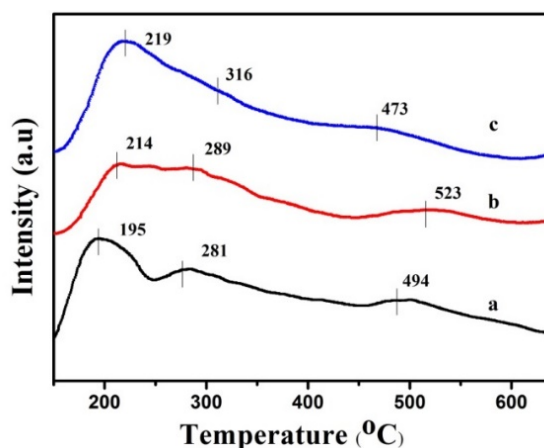


Figure 11. CO_2 -TPD profiles of PtSn/Mg(Al)O with different Mg:Al ratios: (a) $\text{Mg:Al} = 2:1$; (b) $\text{Mg:Al} = 5:1$; (c) $\text{Mg:Al} = 10:1$.

The results in Figures 10 and 11 prove that the acidity and basicity of the catalysts are markedly influenced by the Mg:Al ratio, which influence the properties of the ethane dehydrogenation reaction. Based on previous studies, the increased acidity of catalysts can improve the activity of ethane dehydrogenation, and too much acidity may lead to cracking of products and the deactivation of catalysts due to coking [36]. All these results suggest that a moderate Mg:Al ratio affords the catalyst with the appropriate acidity and basicity, which are beneficial to ethane dehydrogenation reaction.

Results of the catalytic stability test are given in Figure 12. A 700-min ethane dehydrogenation reaction was processed for the PtSn/Mg(Al)O-5 catalyst. From Figure 12a, the initial value of ethane conversion was 21.5%, and the ethane conversion was ultimately maintained above 14% after 700 min.

In Galvita's work, PtSn/Mg(Al)O was used for ethane dehydrogenation, and the catalyst exhibited a rapid loss in conversion activity during the first 40 min. The conversion of ethane to products decreased from approximately 10% to 2.6% for PtSn/Mg(Al)O [37]. In Zhang's work, the ethane conversion of PtSn/Mg(Al)O catalysts decreased from 25% to 8.2%. The percentage of decrease was 66.8% during a 14-h reaction [20]. For the ethane dehydrogenation process in the current study, the results indicate that the catalyst possesses good catalytic stability compared with other works in the literature. The PtSn/Mg(Al)O-5 catalyst possessed a relatively high ethylene selectivity (>98.5%) during the initial stage, and possessed nearly 100% selectivity after the entire 700-min dehydrogenation reaction (Figure 12b).

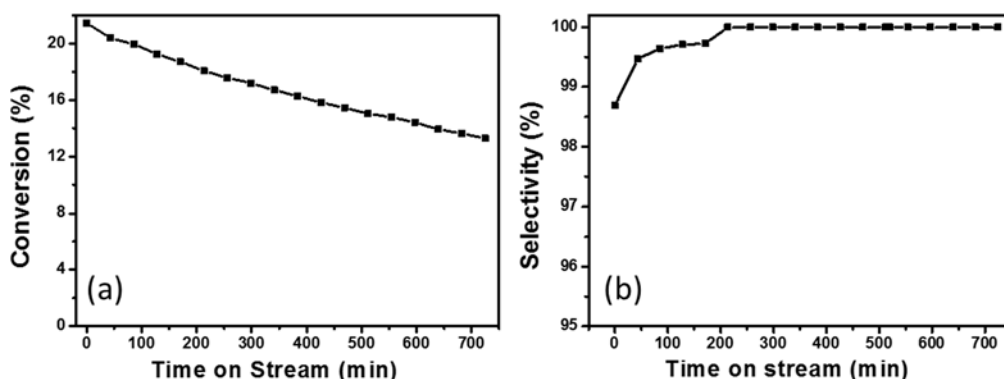


Figure 12. Stability test of PtSn/Mg(Al)O-5 during (a) C_2H_6 conversion, and (b) C_2H_4 selectivity.

Figure 13 displays the PtSn/Mg(Al)O-5 catalyst before and after the C_2H_6 dehydrogenation reaction. Figure 13a,b show the SEM images of PtSn/Mg(Al)O-5 before C_2H_6 dehydrogenation reaction, and Figure 13d,e show the SEM images of PtSn/Mg(Al)O-5 after C_2H_6 dehydrogenation. The morphology indicates that clusters of aggregate crystal particles formed from the flake structure after calcination. Figure 13c,f show the TEM images of PtSn/Mg(Al)O-5 before and after the C_2H_6 dehydrogenation reaction. The PtSn metal particles were dispersed uniformly on the surface of the support before the reaction. The TEM image in Figure 13f shows that a large quantity of coke carbon was generated after C_2H_6 dehydrogenation. The thickness of the generated amorphous carbon layer was nearly 40 nm. Figure 13g,h provide energy dispersive X-ray (EDX) element mapping images of PtSn/Mg(Al)O-5 before and after C_2H_6 dehydrogenation. The distribution of magnesium and aluminum were uniform on the support before and after ethane dehydrogenation. The distributions of platinum and tin appear dispersive, indicating a uniform distribution of the metal particles. Furthermore, it can be seen from the mapping images in Figure 12g,h that the formation of carbon obviously increased after the reaction. The main reason for the deactivation of the catalyst is carbon deposition onto the catalyst surface.

To identify the loss of carbon from the gas stream due to coke formation, the carbon balance was calculated from the ratio of the overall hydrocarbon amounts after the reaction to the initial ethane amount. High carbon balances (96.1%, 96.5%, and 98.8%) were obtained over the PtSn/Mg(Al)O-2, PtSn/Mg(Al)O-5, and PtSn/Mg(Al)O-10 catalysts, respectively, at 120 min, indicating that the majority of ethane was dehydrogenated during the reaction, with some loss of carbon due to coke formation.

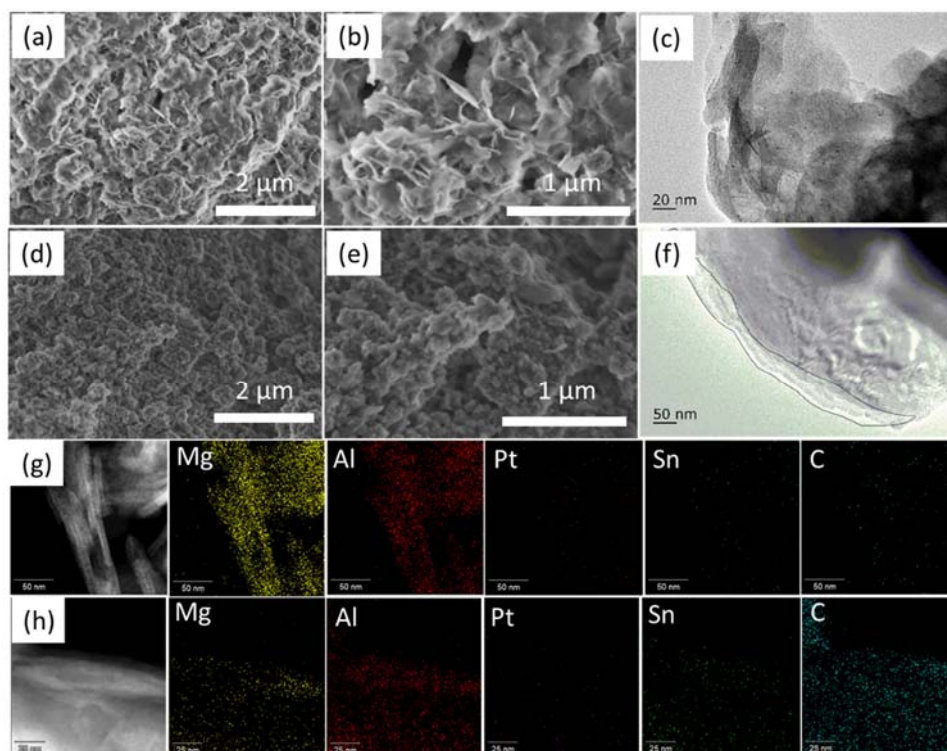


Figure 13. (a,b) SEM images and (c) TEM images of PtSn/Mg(Al)O-5 before the C_2H_6 dehydrogenation reaction; (d,e) SEM images and (f) TEM images of PtSn/Mg(Al)O-5 after the C_2H_6 dehydrogenation reaction; (g,h) energy dispersive X-ray (EDX) element mapping images of PtSn/Mg(Al)O-5 before and after C_2H_6 dehydrogenation.

It was reported that coke formation is related to the behavior of ethylene absorbed onto the active sites of the catalyst, and that strong acidity can promote carbon deposition [1,2]. Our results show that the total acidity of the catalysts decreased with an increase in Mg:Al molar ratio. This is due to the presence a greater proportion of Al, thus generating more acid sites. The increase in the number of acid sites on the catalyst can improve the dehydrogenation performance; however, it can also lead to deep cracking of dehydrogenation products, which enables carbon inactivation of the catalysts. Thus, a moderate Mg:Al ratio is best suited for ethane dehydrogenation.

3. Materials and Methods

Synthesis of Mg(Al)O LDH: Hydrotalcites were synthesized using the co-precipitation method. Different molar ratios of $Mg(NO_3)_2 \cdot 6H_2O$ (Macklin Co., AR., Shanghai, China) (3.33 g, 4.17 g, and 8.33 g) and $Al(NO_3)_3 \cdot 9H_2O$ (Macklin Co., AR., Shanghai, China) (2.57 g) were dissolved in 70 mL of deionized water. NaOH (Sinopharm Chemical Reagent Co., AR., Shanghai, China) and Na_2CO_3 (Sinopharm Chemical Reagent Co., AR., Shanghai, China) were also dissolved in deionized water in another beaker, before adding the two solutions dropwise to the third beaker with some deionized water. The solution was stirred vigorously at room temperature. The resulting suspension was aged overnight at 100 °C, before being filtered and washed with deionized water. It was then dried at 100 °C for 24 h.

Synthesis of PtSn/Mg(Al)O catalysts via the anion exchange method: PtSn/Mg(Al)O was prepared via the anion exchange method. Using a typical procedure, the hydrotalcite (LDH) was exchanged in a mixed solution of K_2PtCl_6 (Aladdin Reagents (Shanghai) Co., Ltd., Shanghai, China) and Na_2SnO_3 (Aladdin Reagents (Shanghai) Co., Ltd., Shanghai, China) at 70 °C for 24 h with moderate

stirring. The resulting solution was filtered and washed with deionized water, and was then dried at 100 °C overnight, before being reduced in H₂/N₂ (10 vol.%) at 873 K for 3 h.

Ethane dehydrogenation: Ethane dehydrogenation was carried out in a fixed-bed quartz reactor with an inner diameter of 8 mm under atmospheric pressure. The catalyst (0.1 g of PtSn/Mg(Al)O after anion exchange) was diluted with 0.5 g of quartz particles, with sizes ranging from 0.25–0.5 mm. The mixed catalysts were put in the center of the quartz tube, before being reduced in a 10% H₂/N₂ atmosphere at 873 K for 3 h. The ethane dehydrogenation reaction was performed in a 10% C₂H₆/N₂ atmosphere at 823 K. The reaction products were analyzed using gas chromatography (GC; Agilent 7890 B, Agilent, Santa Clara, CA, USA) equipped with two thermal conductivity detectors (TCDs) and a flame ionization detector (FID). The FID was used to measure the concentrations of all organic compounds, including CH₄, C₂H₆, and C₂H₄. One TCD was used to measure the concentrations of N₂, and the other was used to quantify the concentrations of H₂.

Ethane conversion and ethane selectivity were defined as follows:

$$\text{C}_2\text{H}_6 \text{ conversion} = \frac{\text{C}_2\text{H}_6 \text{ in} - \text{C}_2\text{H}_6 \text{ out}}{\text{C}_2\text{H}_6 \text{ in}} \times 100\%; \quad (1)$$

$$\text{C}_2\text{H}_4 \text{ selectivity} = \frac{\text{C}_2\text{H}_4 \text{ out}}{\text{C}_2\text{H}_6 \text{ in} - \text{C}_2\text{H}_6 \text{ out}} \times 100\%, \quad (2)$$

where C₂H₆ in and C₂H₆ out are the ethane content in the feed and exit gases, respectively, and C₂H₄ out is the ethylene content in the exit gas.

The carbon balance was calculated as follows:

$$\text{Carbon balance} = \text{C}_x\text{H}_y(\text{out})/\text{C}_2\text{H}_6(\text{in}) \times 100\%. \quad (3)$$

Catalyst characterizations: The SEM images were obtained using a field-emission scanning electron microscope (SEM; SU-70, Hitachi Corporation, Tokyo, Japan) operated at 5 kV. The TEM images were obtained using a transmission electron microscope (TEM; JEM-2010F, JEOL, Tokyo, Japan) operated at 120 kV. The XRD analysis was characterized by an X'Pert Pro MPD diffractometer (PW 3040/60, PANalytical, Almelo, Netherlands) with a scan rate of 5°/min. It was operated at 40 kV, and the applied current was 100 mA. The Brunauer–Emmett–Teller (BET, Quantachrome, Boynton Beach, FL, USA) surface area characterizations were measured via N₂ adsorption–desorption using an ASI QMO002-2 analyzer (Quantachrome, Boynton Beach, FL, USA). The average pore diameters were calculated using the Barrett–Joyner–Halenda (BJH) pore-size model. Temperature-programmed desorption experiments (NH₃-TPD and CO₂-TPD) were performed with a CPB-1 analyzer (Quantachrome, Boynton Beach, FL, USA). The ICP-AES analyses were carried out with an inductively coupled plasma atomic spectrometer (ICPS-8100, Shimadzu, Japan).

4. Conclusions

Mg(Al)O supports were synthesized with three different Mg:Al molar ratios, and bimetallic PtSn catalysts were loaded onto the supports via the anion exchange method. The properties of ethane dehydrogenation of the PtSn/Mg(Al)O catalysts were investigated. The structure and property of the PtSn-Mg(Al)O catalysts were influenced by the Mg:Al molar ratios of the hydrotalcites, which consequently influenced the ethane dehydrogenation performance. The highest ethane conversion and nearly 99% ethylene selectivity were obtained for the PtSn/Mg(Al)O-5 catalyst. The Mg(Al)O catalyst with an Mg:Al ratio of 5: 1 had the largest pore volume and optimal acid–base properties.

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