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## Facile one-pot synthesized ordered mesoporous Mg-SBA-15 supported PtSn catalysts for propane dehydrogenation

Bing Li<sup>a</sup>, Zhenxin Xu<sup>b</sup>, Fangli Jing<sup>a</sup>, Shizhong Luo<sup>a,\*</sup>, Wei Chu<sup>a,\*</sup>

*a.* Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China.

*b.* Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR 7515 CNRS-Université de Strasbourg (UdS), 25, rue Becquerel, 67087 Strasbourg Cedex 08, France.

\*Corresponding authors: Shizhong Luo: <u>luosz@scu.edu.cn</u> Wei Chu: <u>chuwei1965@ scu.edu.cn</u> Tel.: +86 28-85403836; Fax: +86 28-85461108.

## **Graphical Abstract**



#### Highlights

◆ A series of high-surface area and well-ordered mesoporous Mg-incorporated SBA-15 (Mg-SBA-15) were prepared using a one-pot hydrothermal synthesis method.

◆Incorporation of magnesium modified the structural characteristics of the metallic phase and strengthened the interactions of platinum, tin species and support.

◆The existence of Mg stabilized the oxidation states of Sn and facilitated the transfer of the carbon deposits from the active metal to the support.

◆The significant improvements in conversion and selectivity were obtained on the catalyst incorporated with appropriate content of magnesium.

#### Abstract:

A series of high-surface area and well-ordered mesoporous Mg-incorporated SBA-15 (xMg-SBA-15, x=0, 1, 2, 4 and 6) was prepared using a facile one-pot hydrothermal synthesis method. The resulting materials were used to disperse Pt, Sn particles and further studied the catalytic performance for propane dehydrogenation. The physicochemical properties of the supports and catalysts were characterized by XRD, N<sub>2</sub> adsorption-desorption, FT-IR, TEM, NH<sub>3</sub>-TPD, XPS, H<sub>2</sub>-TPD and TG-DTA techniques. Compared with the sample synthesized by the impregnation method, the xMg-SBA-15 materials showed a better Mg species distribution and higher specific surface area. It was found that incorporation of appropriate amounts of Mg promoted the dispersion of metallic nanoparticles and facilitated the transfer of the carbon deposits from the active metal to the support. Such a modification of support not only enhanced the interaction of the Sn-support, but also stabilized the oxidation state of Sn species, leading to the improvement of catalytic activity and stability. The significant increases in conversion and selectivity were obtained on the modified catalysts with appropriate content of Mg. The best catalytic performances were obtained on PtSn/2Mg-SBA-15 catalyst with 2 wt.% of magnesium, showing a higher than 98% selectivity toward propene at a 38.0% conversion of propane even after 6 h reaction.

**Keywords:** Propane dehydrogenation; one-pot hydrothermal synthesis; Mg-incorporated SBA-15; PtSn catalyst; structure-activity relationships;

#### 1. Introduction

As a kind of important industry material, propene has been widely implemented in industrial processes for the production of polypropene, polyacrylonitrile, acrolein, and acrylic acid etc. At present, the effective routes for producing propene mainly contain steam cracking and fluidized catalytic cracking of naphtha.[1, 2] Since the traditional production modes are unable to satisfy the increasing requirement for propene, propane dehydrogenation as one of the most promising approach has gained much attention.[3, 4] Dehydrogenation of low-cost hydrocarbons to corresponding value-added olefins makes this route more economic dominance.[5] Propane dehydrogenation is a highly endothermic and equilibrium limited reaction, meaning higher temperature and lower pressure conditions are needed to accomplish a considerable propene yield.[6] Unfortunately, these demanding conditions facilitate side reactions such as cracking and coke deposition, resulting in the deactivation of catalysts. Therefore, the development of new types of catalysts with high efficiency under these severe reaction conditions is an important subject in this field.

Pt-based catalyst has been broadly applied in alkane dehydrogenation reaction, owing to its excellent ability in activating C-H bonds and conserving simultaneously the C-C bonds.[7, 8] However, carbon deposition and metallic sintering are still the crucial issues in affecting the long term catalytic stability. Coke deposits derive from polymerization of propene or carbon intermediates, which usually occurs at acidic sites located on the support and metal nanoparticles.[9] To our best knowledge, supported PtSn catalyst displays good catalytic performances in propane dehydrogenation process and attracts widely attention. Generally, the properties of PtSn catalysts closely related to the interaction between Pt and Sn, the chemical state of Sn and the features of support.[10, 11] The specific functions of tin were expressed as geometric and electronic modification of platinum phase.[12] It was proposed that Sn promoter decreased the size of surface Pt ensembles, therefore restraining the deep dehydrogenation reactions. On the other hand, the electronic effect of Sn can either favor the charge transfer from Sn<sup>n+</sup> to Pt or create a disparate electronic environment

in Pt-Sn alloys.[13] With regard to support, it plays a substantial role for the dispersion of Pt, Sn active sites. PtSn catalysts supported on various materials such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZSM-5, and SAPO-34 have been extensively studied for dehydrogenation of propane.[14-16] Recently, the SBA-15 shows its potential application in catalysis as well as in propane dehydrogenation thanks to the well defined and ordered mesoporous structure. Such unique features make SBA-15 very well suited as host for the confinement and stabilization of Pt nanoparticles, which is beneficial to obtaining higher dispersion of Pt nanoparticles and preventing particles from agglomeration.[17] Therefore, SBA-15 supported PtSn catalysts may be a promising prospect for the dehydrogenation of propane.

The acidity on the PtSn catalyst hinders the desorption of olefins product and extend the retention time on catalyst surface, leading to the further conversion and carbon deposition due to secondary dehydrogenation and isomerization reactions.[18] The secondary dehydrogenation reaction must be suppressed to improve the selectivity of the desired product propene. It is well established that improved propene yield can be achieved by adding alkaline or alkaline earth metals to the catalyst formulation for propane dehydrogenation.[19] A. Bliek *et al.*[20] reported that the existence of alkali-earth metals in Pt-Sn catalyst could not only adapt the acid sites, but also embellish the interaction between the support and the active sites. The addition of Mg on PtSn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was described by Shi *et al.*[21], showing that Mg promoter could improve the distribution of Pt particles and strengthen the interaction among Pt, Sn, and support, leading to an enhanced catalytic performance.



Scheme 1. - Schematic synthesis procedures for the Mg-incorporated/supported SBA-15 mesoporous materials

The introduction of alkaline metal and alkaline earth metal in the published literature was mostly loaded through the post-synthesis procedure.[22] This process needed two stages calcination to get the final product, which could cause a non-uniform dispersion of Mg component on the support and a loss in the efficiency of the Mg promoter. Moreover, the additive promoter might clog the mesoporous channel thus decrease the surface area and pore size of SBA-15.[23] In the present paper, we prepared the Mg-incorporated SBA-15 with different magnesium loadings by one-pot method (**Scheme 1**) and used them as supports to disperse Pt, Sn particles. The catalytic activity of these catalysts was tested by propane dehydrogenation. Mg/SBA-15 sample was synthesized using the traditional impregnation method as the referential sample. The differences between these samples on structure-activity relationships were identified and discussed. This can provide us with important information to identify the influence of magnesium promoter on the physicochemical characteristics and catalytic properties of PtSn/SBA-15 in the propane dehydrogenation.

#### 2. Experimental

#### 2.1. Catalyst preparation

The silica mesoporous support SBA-15 and Mg-incorporated SBA-15 were synthesized using a triblock copolymer, Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Aldrich) as a template according to the procedure reported in the literature.[24] The silica source was the tetraethyl orthosilicate (TEOS, 98%). In a typical synthesis, 2 g of P123 was first dissolved in 60 ml of 2M HNO<sub>3</sub> and 15 ml of deionized water to form a clear solution at room temperature. Then a calculated amount of magnesium acetate (Mg(CH<sub>3</sub>COO)<sub>2</sub>) was added to the previous solution under stirring. After 3 h, 4.25 g of TEOS was added dropwise to the solution and continuously stirred for 24 h at 40 <sup>o</sup>C. The resulting suspension was placed into a Teflon-lined autoclave to undergo hydrothermal treatment at 100 °C for 24 h. Finally, the mixture was evaporated under 80  $^{\circ}$ C with stirring and dried at 80  $^{\circ}$ C for 12 h, then calcined at 550  $^{\circ}$ C for 6 h to remove the surfactant and release the pores. The received samples were denoted as xMg-SBA-15 (the nominal mass fraction x = 0, 1, 2, 4 and 6) hereinafter. Another sample was synthesized by the incipient-wetness impregnation method and denoted as xMg/SBA-15-IM. First, the calcined SBA-15 powder was introduced into a calculated amount of Mg(CH<sub>3</sub>COO)<sub>2</sub> aqueous solutions. After impregnation for 12 h, the final mixture was evaporated under 80 °C and then dried and calcined by the same procedure as previously mentioned.

PtSn catalysts were prepared by incipient-wetness impregnation method.  $SnCl_2 \cdot 2H_2O$  and  $H_2PtCl_6 \cdot 6H_2O$  precursors were dissolved in deionized water to form a solution and the solution was impregnated with the support powder. Then, the mixture was sonicated for 30 min and then under static condition for 12 h. After that, the solution was dried at 80 °C for 12 h and calcined at 500 °C for 4 h. The nominal compositions of these catalysts were 1 wt.% Pt and 2 wt.% Sn.

#### 2.2. Catalyst characterization

Low-angle XRD patterns were collected in the  $2\theta$  range of 0.5-10° with a step size of 0.02° using an EMPYREAN diffractometer. Wide-angle XRD patterns were obtained by an X-ray diffraction apparatus (Philips X' pert PRO) using Cu Ka (45 kV, 50 mA) radiation.

The nitrogen adsorption-desorption isotherms were measured at -196  $^{\circ}$ C on an automated surface area & pore size analyzer (Quadrasorb SI apparatus). Before each measurement, the samples were outgassed under vacuum at 300  $^{\circ}$ C for 3 h.

The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer at room temperature. The spectra were collected in the range of 4000-400 cm<sup>-1</sup> and KBr was used as background.

The X-ray photoelectron spectra (XPS) were achieved on the XSAM800 spectrometer with an Al K $\alpha$  (hv = 1486.6 eV) X-ray source and the binding energies were amended by using C (1 s) at 284.6 eV as an internal standard.

The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) measurements were implemented by a Micromeritics AUTOChem II2920 instrument to analyze the acidity of the catalysts. The sample (100 mg) was pretreated at 250 °C for 2 h under a helium flow (30 ml/min) before being cooled to 50 °C and saturated with adsorbed ammonia. During desorption, a thermal conductivity detector (TCD) was employed to record the TPD profiles from 50 to 900 °C with a heating rate of 10 °C /min.

The temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPD) was measured over a Quantachrome Autosorb-1 instrument equipped with a TCD detector. The catalyst (100 mg) was first reduced in situ in a 10 % H<sub>2</sub>/N<sub>2</sub> mixture gas flow of 30 ml/min, with a 10 °C/min ramping rate from 30 °C to 500 °C and maintained at that temperature for 1 h. After that, the catalyst was cooled to 30 °C and subjected to H<sub>2</sub>-saturation in a stream of 10 % H<sub>2</sub>/N<sub>2</sub>. Then, the sample was purged with nitrogen for 3 h to remove H<sub>2</sub> in the gas phase, and then was heated from 30 °C to 800 °C with a ramping rate of 10 °C /min.

Transmission electron micro-scope (TEM) images were taken on JEOL JEM 2010 electron micro-scope at an acceleration voltage of 120.0 kV. The samples were ultrasonic treatment and well suspended in ethanol. Drops of the suspension were employed and well dispersed on a copper grid.

The thermogravimetric analysis was performed with a TGA Q500 thermogravimetric analyzer. The samples were heated under air atmosphere from room temperature to 750 °C at a heating rate of 10 °C /min.

#### **2.3. Catalytic performance**

The propane dehydrogenation reaction was performed in a fix-bed quartz tubular reactor with an inner diameter of 8 mm. The catalyst (0.2 g) was placed into the center of the reactor and reduced in H<sub>2</sub> at 500 °C for 1 h before catalytic evaluation. The reaction conditions were as follows: 580 °C of reaction temperature, atmospheric pressure,  $C_3H_8/Ar= 7:3$  (molar ratio) and the propane weight hourly space velocity (WHSV) is 8.25 h<sup>-1</sup>. The reaction products were analyzed on-line using a GC-3000B model gas chromatography equipped with a thermal conductivity detector (TCD). The conversion of propane and the selectivity for propene were defined using following equations:

Propane conversion(%) = 
$$\frac{F_{C_3H_8,in} - F_{C_3H_8,out}}{F_{C_3H_8,in}} \times 100\%$$
 (1)

Propene selectivity(%) = 
$$\frac{F_{C_3H_6,out} - F_{C_3H_6,in}}{F_{C_3H_8,in} - F_{C_3H_8,out}} \times 100\%$$
 (2)

Where  $F_{i,in/out}$  is the flow rate of each component in the feed or effluent.

#### 3. Results and discussion

#### 3.1. Characterization of Mg-modified SBA-15 supports



Fig. 1 - (a) Low-angle and (b) wide-angle XRD patterns of different supports: (A) SBA-15, (B) 1Mg-SBA-15, (C) 2Mg-SBA-15, (D) 4Mg-SBA-15, (E) 6Mg-SBA-15, and (F) 2Mg/SBA-15-IM

The low-angle XRD patterns of SBA-15 and Mg-modified SBA-15 samples are shown in **Fig. 1(a)**. The XRD pattern of SBA-15 showed a sharp peak at about  $0.92^{\circ}$  together with two additional weak peaks, which were indexed to (100), (110), and (200) reflections, respectively. The XRD profile verified the formation of typical hexagonally-structured SBA-15 silica with highly ordered mesoporous channels as reported by Zhao *et al.*[24] All of the patterns of xMg-SBA-15 exhibited these three peaks with high intensity, indicating that the hexagonal mesostructure was intact even if magnesium was introduced. Wei *et al.*[25] succeeded in synthesizing the well-ordered structure MgO/SBA-15 composites since Mg<sup>2+</sup> ions were known to

interact strongly with the non-ionic surfactant P123. The intensity of diffraction peaks showed gradual decrease with the introduction of Mg component, suggesting that there was a deterioration of the ordered pore structures.[26] The calculated unit cell parameters ( $a_0$ ) corresponding to the  $d_{100}$  spacings in the XRD pattern are listed in **Table 1**. It could be observed that the unit cell parameter  $a_0$  of SBA-15 was 10.7 nm while that was 10.7-10.9 nm for the magnesium-doped samples, indicating the symmetry of pore structure did not significantly alter.

The wide-angle XRD patterns for these materials are depicted in **Fig. 1(b)**. All of the patterns showed a broad peak in  $2\theta$  region of 20-30°, corresponding to the typical reflection of amorphous silica.[27] Except the typical patterns of SBA-15, the peaks at  $2\theta$  of 42.9° and 62.3° were observed in 2Mg/SBA-15-IM sample, which indexed to reflections of magnesium oxide (PDF Card No. 45-0946).[28] The absence of these XRD diffractions indicated a better dispersion of magnesium species for the xMg-SBA-15 samples synthesized by one-pot method.

Table 1 Textural properties of SBA-15 and Mg-modified SBA-15 materials

Sample	$S_{BET}^{a} (m^2 g^{-1})$	$V_t^{b} (cm^3 g^{-1})$	$V_{mic}^{c} (cm^3 g^{-1})$	$D_p^{d}(nm)$	d <sub>100</sub> <sup>e</sup> (nm)	$a_0^{f}$ (nm)
SBA-15	571.5	0.78	0.10	5.4	9.3	10.7
1Mg-SBA-15	504.4	0.69	0.10	5.5	9.4	10.9
2Mg-SBA-15	420.5	0.65	0.08	6.1	9.3	10.7
4Mg-SBA-15	385.5	0.70	0.05	6.6	9.4	10.9
6Mg-SBA-15	381.0	0.67	0.04	6.6	9.4	10.9
2Mg/SBA-15-IM	343.3	0.61	0.10	5.4	9.4	10.9

<sup>a</sup> BET specific areas.

<sup>b</sup> The total pore volumes were obtained at  $P/P_0 = 0.99$ .

<sup>c</sup> The microporous volume was calculated using the *t*-plot method.

<sup>d</sup> Average pore diameter calculated using the BJH method.

<sup>e</sup> d<sub>100</sub> was the lattice spacing obtained from low-angle XRD.

 $^{\rm f}$  a<sub>0</sub> was the hexagonal unit-cell parameter calculated using the equation: a<sub>0</sub>=2d<sub>100</sub>/ $\sqrt{3}$ .



Fig. 2 - (a) N<sub>2</sub> adsorption-desorption isotherms and (b) BJH pore size distribution of different samples: (A) SBA-15, (B) 1Mg-SBA-15, (C) 2Mg-SBA-15,

#### (D) 4Mg-SBA-15, (E) 6Mg-SBA-15, and (F) 2Mg/SBA-15-IM

The textural properties of the samples were investigated by nitrogen adsorption-desorption and the corresponding isotherms and pore size distributions are shown in **Fig. 2**. All the samples exhibited typical isotherm of type IV with hysteresis loops of type H1 according to the IUPAC classification, indicating the characteristic of mesoporous materials.[29] It should be noted that the isotherms of Mg-modified SBA-15 samples were very similar to that of SBA-15 in shape, suggesting that these materials retained the initial mesoporous texture. The pore size distributions of the support materials (**Fig. 2(b)**) displayed the pore size with high uniformity and mainly distributed in the range of 4-7 nm. The results showed that all of the support materials

exhibited highly ordered mesoporous of the cylindrical channels with a narrow pore size distribution, which was in good consistent with the results obtained by low-angle XRD.

The specific surface area, pore volume and average pore diameter of SBA-15 and Mg-modified SBA-15 materials are summarized in Table 1. The surface areas and total pore volumes of xMg-SBA-15 mesoporous materials decreased gradually with the increasing amount of magnesium in the supports. Magnesium species interacted with silanol groups and formed the Si-O-Mg monolayer, the residual magnesium species covered on the top and converted to the smooth  $MgO_x$  layer after calcination, thus decreasing both the surface area and pore volume.[30] Davidson et al.[31] reported that the silica walls structure of SBA-15 materials was more complex and showed a "corona" region with microporous around the cylindrical organic aggregates due to the partial occlusion of the PEO chains in the silica matrix. Magnesium species incorporated in SBA-15 would partly fill the "microporous corona". Therefore, the average pore diameter increased while the micropore volume decreased when magnesium amount changed from 1wt.% to 6wt.%. Meanwhile, 2Mg/SBA-15-IM possessed the lowest surface area and pore volume value, indicating that the one-pot method was better able to maintain the mesoporous structure of silica materials.



Fig. 3 - FT-IR spectra of samples: (A) SBA-15, (B) 1Mg-SBA-15, (C)

#### 2Mg-SBA-15, (D) 4Mg-SBA-15, (E) 6Mg-SBA-15

Infrared spectroscopy was used to characterize the surface property of the as-made materials, the spectra were collected in **Fig. 3**. It could be clearly seen that the framework vibrations of xMg-SBA-15 were characteristically similar to those of SBA-15 structure. The symmetric stretching mode showed at 804 cm<sup>-1</sup>, while the band at 463 cm<sup>-1</sup> was assigned to the Si-O-Si bending mode.[32] The band in the range of 1050-1100cm<sup>-1</sup> was related to characteristic of Si-O-Si vibrational stretching, and the peak in the samples was somewhat red-shifted as the amount of incorporated magnesium increased, which indicated the interaction between magnesium and silicon.[33]



Fig.4 - TEM images of 2Mg-SBA-15: (a) taken along the [001] directions and (b) taken along the [110] directions; (c and d) HAADF-STEM image of 2Mg-SBA-15 and EDS elemental mapping images of O, Si, and Mg

To investigate the morphology of Mg-incorporated SBA-15 and the distribution of magnesium species, TEM analyses were carried out. 2Mg-SBA-15 sample (**Fig.** 4(a, b)) exhibited highly ordered hexagonal structure with narrow pore diameter size distribution, which was in accordance with the XRD and N<sub>2</sub> adsorption-desorption

results. There was no MgO particles observed on the 2Mg-SBA-15 material surface or pores, indicating the well dispersion of magnesium on the support. The homogeneous dispersion of Mg species in SBA-15 led to the less-blocked mesopores, consequently these samples prepared by *in situ* incorporating method displayed the higher surface area, pore diameter and pore volume than the impregnated sample. Distribution of Mg on the support was confirmed by means of HAADF-STEM combined with EDS elemental mapping analysis. From the elemental mapping images, it was clear that O, Si and Mg were evenly distributed in mesoporous structure.



#### 3.2. Characterization of PtSn catalysts

Fig. 5 - (a) Low-angle and (b) wide-angle XRD patterns of reduced catalysts: (A) PtSn/SBA-15, (B) PtSn/1Mg-SBA-15, (C) PtSn/2Mg-SBA-15, (D)

#### PtSn/4Mg-SBA-15, (E) PtSn/6Mg-SBA-15, and (F) PtSn/2Mg/SBA-15-IM

XRD patterns of reduced PtSn/xMg-SBA-15 and PtSn/2Mg/SBA-15-IM samples are shown in **Fig. 5**. From low-angle XRD patterns, the features of all the samples were rather similar, with three well-resolved diffraction peaks that indexed to (100), (110) and (200) reflections, indicating the hexagonal mesostructure was intact even after loading Pt and Sn. Wide-angle XRD patterns showed the typical peak of amorphous silica at  $2\theta = 23.5^{\circ}$ . The XRD reflections of  $40.0^{\circ}$ ,  $46.3^{\circ}$ ,  $67.4^{\circ}$  and  $80.8^{\circ}$ at  $2\theta$  could be assigned to inter-planar spacing (111), (200), (220) and (311) of cubic Pt metal structure, respectively.[34] There was no peak of Sn or SnO<sub>x</sub>, probably due to the highly-dispersed Sn species or the formation of amorphous SnO<sub>x</sub> phases.



Fig. 6 - TEM images of the reduced samples: (a, b) PtSn/SBA-15, (c)PtSn/2Mg-SBA-15, and (d) PtSn/2Mg/SBA-15-IM

To further investigate the morphology of the catalysts and the effect of Mg on the modification of catalysts, the TEM experiments were implemented. The TEM images of the corresponding samples (**Fig. 6**) showed that all catalysts remained the highly ordered structure after Pt and Sn loading. For PtSn/SBA-15 sample, metallic particles

were irregularly distributed on the whole support and some particles were confined in the porous channel appeared in Fig. 6(a), while some agglomerated particles distributed on the external surface of the catalyst and the ends of mesopores were partially blocked by the large particles. The movement of Pt particles within the pore channels or from pores to the surface of support could occur under the reduction conditions because of the weak interaction between Pt and support. The agglomeration of metallic particles resulted in the low accessible metal surface area, which in consequence suppressed the catalytic ability to adsorb the hydrogen at low temperature.[35] Meanwhile, for the Mg-decorated samples, no large aggregates of the metals on the external surface were observed, indicating a high distribution throughout the pores of Pt and Sn metallic particles. The results suggested that the modification of Mg could markedly influence metallic nanoparticles distribution. This could be explained by that suitable content of magnesium additives could prevent the agglomeration of dispersed Pt into discrete particles, thus an increase in platinum dispersion was observed.[36] It was noted that the surfaces of PtSn/2Mg/SBA-15-IM sample seemed to be covered by dark clouds, which could be caused by the unequally dispersion of Mg species and be further responsible for the decline in both pore volume and surface area. The results were in accord with the textural properties characterized by nitrogen adsorption-desorption (Table 1).



Fig. 7 - NH<sub>3</sub>-TPD profiles of different catalysts: (A) PtSn/SBA-15, (B)

#### PtSn/2Mg-SBA-15, and (C) PtSn/2Mg/SBA-15-IM

**Fig. 7** shows the NH<sub>3</sub>-TPD profiles of different catalysts. There were two desorption peaks for each sample: the first desorption peak at about 60-230 °C and the second one at above 230 °C. The first peak was attributed to the desorption of the adsorbed NH<sub>3</sub> on the weak acid sites, whereas the second peak was assigned to the moderate acid sites.[37] In a comparison, a distinct decrease of ammonia desorption at low temperature and the sharply decreased ammonia desorption peak at high temperature were observed after loading of magnesium component. This phenomenon showed that the catalyst acidity decreased with the addition of magnesium, which could increase catalytic selectivity and stability.



## Fig. 8 - (a) Pt 4f and (b) Sn 3d<sub>5/2</sub> XPS spectra corresponding to the reduced catalysts: (A) PtSn/SBA-15, (B) PtSn/2Mg-SBA-15, (C) PtSn/6Mg-SBA-15, and (D) PtSn/2Mg/SBA-15-IM

photoelectron X-ray spectroscopy conducted the reduced was on PtSn/xMg-SBA-15 catalysts to further study the electronic properties of the surface elements. Fig. 8(a) shows the XPS spectra corresponding to the Pt 4f of the reduced catalysts. The binding energies at 71.2 and 74.5 eV could be assigned to Pt<sup>0</sup>, only metallic Pt species presented on the catalysts. A slight shift to higher binding energy was appeared as magnesium incorporated, which could be due to the strong metal-support interaction (SMSI) between Pt and xMg-SBA-15 supports, it was conducive to make Pt species with better resistance of sintering. Fig. 8(b) shows the XPS spectra corresponding to the Sn  $3d_{5/2}$  region. Three peaks were obtained at 485.9, 486.6 and 487.2 eV after deconvolution treatment, corresponding to different types of tin species. The binding energy at 485.9 eV was associated with a reduced tin phase, either in the metallic  $(Sn^0)$  or in the alloy state.[38] While the second and third peak were attributed to different types of oxidized Sn i.e. Sn<sup>2+</sup> and/or Sn<sup>4+</sup>. It was well established that  $Sn^{2+}$  and  $Sn^{4+}$  could not be discriminated since their binding energies were very close.[10]

Sample	Binding energy (eV)						Sn <sup>0</sup> /Sn <sup>Tol</sup>	Pt	Sn		
	Pt 4f		Sn 3d <sub>5/</sub>	2		Mg 2p	Si 2p	O 1s	(%) <sup>a</sup>	wt.%	<sup>b</sup> wt.% <sup>b</sup>
PtSn/SBA-15	71.2	74.5	485.9	486.6	487.2		103.3	532.5	14.1	0.69	1.80
PtSn/2Mg-SBA-15	71.4	74.6	486.0	486.7	487.5	50.5	103.0	532.3	6.5	0.86	1.93
PtSn/6Mg-SBA-15	71.6	75.0	486.0	486.7	487.4	50.6	102.9	532.2	9.0	0.80	1.84
PtSn2Mg/SBA-15-IM	71.3	74.5	486.0	486.7	487.2	50.4	103.1	532.3	8.1	0.79	1.83

Table 2 The binding energy and surface composition of catalysts derived from **XPS** analysis

<sup>a</sup> Calculated using the peak area.

<sup>b</sup> The mass percent of surface Pt and Sn elemental on the catalysts.

The binding energies of surface elements Pt 4f, Sn3d<sub>5/2</sub>, Mg 2p, Si 2p and O 1s for various catalysts were summarized in Table 2. Mostly amount of the Sn species were in the oxidized state. What's more, the content of Sn<sup>0</sup> species in PtSn/SBA-15 catalyst (14.1%) was much more than that of the Mg-modified samples, indicating that more amounts of tin existed in a non-metallic state (Sn<sup>2+</sup> or Sn<sup>4+</sup>) after magnesium was added. However, an excess of Mg loading (6 wt.%) weakened the interaction between Sn species and support, resulting in the increase of metallic tin content. Thus, it could be concluded that a proper amount of Mg addition would strengthen the Sn-support interaction, then inhibit the exhaustive reduction of tin species and stabilize the oxidized tin species. It was found that the oxidative Sn species  $(Sn^{4+} \text{ or } Sn^{2+})$  could modify the electronic and geometric properties of Pt species, leading to the great reactivity and stability.[39] The mass percent of surface Pt and Sn (Table 2) showed that incorporation of magnesium in SBA-15 enhanced the dispersion of Pt and Sn species on the catalysts surface.[40] Meanwhile, much stronger interactions of Pt, Sn and supports were observed over PtSn/2Mg-SBA-15 in comparison with the impregnated sample. In addition, the binding energy of Mg 2p over PtSn/2Mg/SBA-15-IM was smaller than that over PtSn/xMg-SBA-15, while it was opposite for Si 2p. This might be caused by the formation of MgSiO<sub>3</sub> over PtSn/xMg-SBA-15 samples.[41]



# Fig. 9 - H<sub>2</sub>-TPD profiles of the catalysts after reduction at 500 °C: (A) PtSn/SBA-15, (B) PtSn/1Mg-SBA-15, (C) PtSn/2Mg-SBA-15, (D) PtSn/4Mg-SBA-15, (E) PtSn/6Mg-SBA-15, and (F) PtSn/2Mg/SBA-15-IM

The H<sub>2</sub>-TPD profiles of the reduced catalysts are displayed in Fig. 9, where two hydrogen desorption peaks could be observed in the profiles. In general, the desorption peak at low temperature (84-125 °C) was attributed to the hydrogen on metallic Pt, whereas the high temperature desorption peaks at 650 °C could be assigned to spillover hydrogen.[22, 42] The amount of H<sub>2</sub> desorption for different catalysts is shown in Table 3. In the case of magnesium promoted catalysts, the main difference originated from the hydrogen desorption at low temperature, as the amount of hydrogen was up to 94  $\mu$ l/g<sub>cat.</sub> regardless of the magnesium content in the catalysts. Meanwhile, the corresponding temperature moved towards the higher temperature, revealing that the capacity of absorbing  $H_2$  became much stronger at low temperature. It was worthy noting that the PtSn/SBA-15 sample showed the least amounts of hydrogen adsorbed compared with that of the Mg-SBA-15 based catalysts, which was probably caused by the diminished Pt particles because of sintering. Generally, the main reason for the decrease in amounts of hydrogen on metallic Pt was the sintering of particles.[43] According to the hydrogen desorption behaviour at low temperature, one can conclude that Pt particles dispersed well on catalyst surface, which would provide accessible metal surface area for the dehydrogenation of propane.[35] Nevertheless, when the concentration of magnesium was excessive (6 wt.%), more amounts of magnesium species might block the platinum particles, which led to the decrease of the metal dispersion. [44, 45] These results suggested that the promoter Mg could make a significant difference in metallic distribution. Moreover, the catalyst with modified Mg species by the one-pot method possessed higher metal dispersion than that by the impregnation method.

#### Table 3 The amount of different hydrogen desorption for the reduced catalysts

Sample	H <sub>2</sub> uptake ( $\mu$ l/g <sub>cat.</sub> )					
	84-125 °C	650 °C	Total			
PtSn/SBA-15	13.5	38.5	52.0			
PtSn/1Mg-SBA-15	36.6	38.9	75.5			
PtSn/2Mg-SBA-15	53.2	38.4	91.6			
PtSn/4Mg-SBA-15	93.8	40.4	134.2			
PtSn/6Mg-SBA-15	81.4	38.9	120.3			
PtSn/2Mg/SBA-15-IM	44.2	38.2	82.4			

## 3.3. Catalytic performance for propane dehydrogenation and coke analysis



Fig. 10 - (a) Propane conversion and (b) propene selectivity as functions of time on stream for different catalysts (reaction conditions: T = 580 °C,  $C_3H_8$ :Ar = 7:3 (molar ratio), 0.1 MPa, WHSV = 8.25 h<sup>-1</sup>; m(cat) = 0.2 g)

**Fig. 10** shows the catalytic performance of propane dehydrogenation over the different catalysts. For PtSn/SBA-15 catalyst, the initial conversion of propane was 35.7% and then reduced to 27.2% after 6 h reaction. The catalytic activity and stability were clearly enhanced when 1-4 wt.% Mg was introduced into the catalysts. Nevertheless, the catalytic activity declined rapidly with the further increase of Mg, suggesting that excess Mg content would suppress the propane dehydrogenation

reaction. The promotion effect of Mg on the catalytic performance could be related to the better metallic particle distribution and stabilized effect of nonmetallic state Sn species. The influence of preparation method was also dramatic, PtSn/2Mg-SBA-15 prepared by one-pot method exhibited better catalytic activity than PtSn/2Mg/SBA-15-IM. At the same time, the PtSn/2Mg-SBA-15 catalyst showed the most excellent catalytic activity with a maximum initial propane conversion of 43.0% among all the samples.

**Fig. 10(b)** shows propene selectivity versus reaction time for different catalysts. It could be observed that the propene selectivity kept stable for 6 h propane dehydrogenation reaction. With the incorporation of Mg (1-4 wt.%), the propene selectivity for other catalysts were markedly higher than that of PtSn/SBA-15 catalyst, and stabilized at above 95.0%. The PtSn/2Mg-SBA-15 catalyst showed the highest propene selectivity reached 99.2% among all catalysts. As for PtSn/SBA-15 sample, some metal particles were agglomerated due to the weak interaction among Pt, Sn and support (**Fig. 6(a)**). Hydrogenolysis reaction would be carried out easily since this unwanted side reaction needed relatively large platinum ensemble, which resulted in a low selectivity of propene.[46] However, the continuous addition of Mg (6 wt.%) resulted in the decreased propene selectivity compared with that of the PtSn/SBA-15 catalyst.

It is known that platinum was the only active metal in PtSn/SBA-15 catalyst and propene was formed only by dehydrogenation on the metallic sites, while the main by-products (C1-C2 hydrocarbons) were mainly from propane cracking on the support.[47] Therefore, the changes of acidity and Pt active sites were responsible for the selectivity of propene. The addition of Mg promoted metal dispersion and decreased the acidity of the catalyst, inhibiting the side reactions, so a better catalyst performance was obtained. On the other hand, it was widely reported that two types of Pt active sites existed in the PtSn catalyst, denoted as  $M_1$  sites and  $M_2$  sites.[48] Platinum directly anchored on the support surface formed multiple Pt centers i.e.  $M_1$ sites, while Pt particles attached to the SnO<sub>x</sub> surface with a "sandwich structure" were assigned to the  $M_2$  sites. Generally,  $M_1$  sites were connected with the side reactions

such as hydrogenolysis and coking, whereas the  $M_2$  sites were responsible for the dehydrogenation of propane. According to the XPS results, the presence of Mg dramatically restrained the reduction of Sn species and stabilized the oxidation states of Sn, which was favorable to form the  $M_2$  sites. Consequently, more  $M_2$  sites were produced and better catalytic performance was realized.

Concerning the PtSn/6Mg-SBA-15 sample with an excess of Mg loading and PtSn/2Mg/SBA-15-IM introducing of Mg by impregnation method, the decrease in catalytic performance might be due to the changed balance metallic function and a lower percentage of the  $SnO_x$  species. However, with the continuous addition of Mg and the impregnation method both led to a deterioration of the ordered pore structure and decreased the surface area of catalyst, which were damage to the catalytic performance. Table S1 shows the carbon balance for different catalysts, and good balances were obtained.

**Table 4** Values of initial conversion ( $X_0$ ), final conversion ( $X_f$ ), deactivation parameter (*D*) after 6 h reaction, and initial selectivities to olefins at 580 °C for different catalysts

Sample	$X_{ m o}(\%)$	$X_{ m f}$ (%)	$D^{\mathrm{a}}$ .	S <sup>b</sup> (%)			
<b>F</b>				$C_3H_6$	$C_2H_6$	$C_2H_4$	$CH_4$
PtSn/SBA-15	35.9	27.2	24	94.09	1.83	1.28	2.35
PtSn/1Mg-SBA-15	40.9	35.5	13	96.31	0.84	1.26	1.33
PtSn/2Mg-SBA-15	43.0	38.1	11	97.84	0.57	0.63	0.97
PtSn/4Mg-SBA-15	38.3	30.4	20	94.23	0.92	0.96	3.41
PtSn/6Mg-SBA-15	32.8	24.8	24	89.00	3.03	2.18	5.49
PtSn/2Mg/SBA-15-IM	37.5	30.0	20	95.51	1.26	0.62	2.36

<sup>a</sup> The deactivation parameter (*D*) was defined as:  $D = 100 \times (X_0 - X_f)/X_0$ , where  $X_0$  was the initial conversion and  $X_f$  was the final conversion.[45]

<sup>b</sup> The initial major by-product selectivity.

Table 4 shows the percentage of deactivation after 6 h on stream for the catalysts.

It could be observed that appropriate amount of Mg-incorporated in SBA-15 (1 wt.% ~ 4 wt.%) was good to improve the catalytic stability, whereas an excess of Mg loading (6 wt.%) played a negative effect on stability. The stability of the catalysts decreased in the following sequence: PtSn/2Mg-SBA-15 > PtSn/1Mg-SBA-15 > PtSn/4Mg-SBA-15 = PtSn/2Mg/SBA-15-IM > PtSn/6Mg-SBA-15 = PtSn/SBA-15. The initial major by-product selectivity is shown in Table 4. The PtSn/2Mg-SBA-15 catalyst exhibited the lowest by-product selectivity. With the continuous increase of magnesium from 1 to 4 wt.%, the selectivity of by-products significantly decreased, suggesting that the side reactions were well restrained. These results were well in accordance with propene selectivity in Fig. 10(b). Table S2 lists some related literature data over the different Pt catalysts for propane dehydrogenation. Despite differences in catalyst compositions and reaction conditions, the PtSn/2Mg-SBA-15 catalyst used in this study showed better catalytic performance than most catalysts.



Fig. 11 - TEM results for spent catalysts: (a, b) PtSn/SBA-15, (c,

#### d)PtSn/2Mg-SBA-15, (e, f) PtSn/2Mg/SBA-15-IM

The TEM images for the spent catalysts are shown in **Fig. 11**, all of the samples maintained ordered meso-porous structure after 6 h reaction. For the spent PtSn/SBA-15 catalyst, some porous channels were blocked by the deposited carbonaceous species, resulting in the activity loss. The coke formed on catalyst surface not only covered the active sites but also plugged up the channel where the propene outflowed.[11] There was no obvious carbon species was observed on the spent Mg-modified catalysts, and most of the metallic particles were confined within the channels of the porous. The confinement effect from the channel of the SBA-15

molecular sieve would help to stabilize the metallic particles and improve the sintering resistance, which could increase the catalytic stability during the propane dehydrogenation reaction.[49]



Fig. 12 - TG-DTA profiles of spent catalysts: (A) PtSn/SBA-15, (B) PtSn/2Mg-SBA-15, (C) PtSn/6-MgSBA-15, and (D) PtSn/2Mg/SBA-15-IM

As far as catalytic deactivation was concerned, coke deposition was an inevitable issue. The deposited coke could be easily identified and quantified under the help of TG analysis. As shown in **Fig. 12**, there were two successive weight loss regions on the spent Mg-modified catalysts, representing two different coke deposits. The first weight loss at around 250 °C was assigned to the coke deposited on the metal surface, while the weight loss at high temperature (520 °C) corresponded to the coke located on the support.[50] It was clear that for the spent PtSn/SBA-15 catalyst, most of carbon deposits covered the active metal and only a small proportion of them located the external surface of the carrier. In addition, it was important to note that the combustion temperature for the coke on Mg-modified catalysts shifted to the lower temperature, suggesting that the deposited carbon on the surface of metal became more active. These phenomena suggested that the presence of Mg in the catalyst promoted the migration of the coke deposits from the metal sites to the support.

Namely, with the presence of Mg, the role of tin promoter could be reflected more sufficiently. As known to all, the presence of Sn on Pt-Sn catalyst could decrease the size of the surface Pt ensembles (geometric effect), so that the hydrocarbon was unable to form the multiple carbon-metal bonds readily, then the coke precursor was more active and could more easily transfer to the support.[12]

The amount of deposited coke followed the order PtSn/2Mg-SBA-15 (3.9%) < PtSn/2Mg-SBA-15-IM (6.3%) < PtSn/6Mg-SBA-15 (8.0%) < PtSn/SBA-15 (8.4%). In general, olefin was the primary precursor in the mechanism of coke formation and the acid sites of the PtSn/SBA-15 catalyst would result in the increase of carbon deposition.[**51**] Obviously, the change of Pt active sites and catalyst acidity would influence the coke formation. As commented before, suitable addition of magnesium into SBA-15 decreased the catalyst acidity, promoted the dispersion of metallic particles and also strengthened the interactions between platinum, tin species and support. Under the circumstances, the presence of Mg could suppress the side reactions. However, not only the catalyst acidity but also the high proportion of M<sub>1</sub> active sites on the catalyst surface was responsible for the coking reaction. Therefore, the more coke formation was formed since excess introduction of Mg resulted in decreased of these M<sub>1</sub> active sites.

#### 4. Conclusion

Well-ordered mesoporous structures Mg-incorporated SBA-15 materials with 1-6 wt.% of magnesium were prepared by the one-pot synthesis. Compared with Mg/SBA-15-IM from the impregnation method, one-pot synthesized Mg-SBA-15 behaved more stable mesoporous structure of SBA-15 and better Mg species distribution. These materials were further used as PtSn catalyst supports for propane dehydrogenation. It was found that incorporation of appropriate amount of Mg modified the structural characteristics of the metallic phase and strengthened the interactions between platinum, tin species and support. Meanwhile, the presence of magnesium facilitated the transfer of the carbon deposits from the active metal to the

support surface. In addition, the existence of Mg enhanced the Sn-support interaction and stabilized the oxidation states of Sn, which would heighten the effect of tin promoter. While excessive Mg weakened the Sn-support interaction and decreased the catalytic performance. In our experiment, the PtSn catalysts with 1-4 wt.% Mg dopant exhibited better catalytic activity for propane dehydrogenation than PtSn/SBA-15 sample. The PtSn/2Mg-SBA-15 sample with 2 wt.% Mg synthesized by one-pot method showed the most excellent catalytic activity with a propane conversion of 43.0% and a propene selectivity of 99%.

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