

Effects of Mg, Ca, and K Addition on Pt-Sn/ γ -Al₂O₃ for Propane Dehydrogenation

Naseri, Maryam

Department of Chemistry Engineering, Iran University of Science and Technology,
P.O. Box 16846-13114 Tehran, I.R. IRAN

Tahriri Zangeneh, Farnaz

Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company,
P.O. Box 14358-84711 Tehran, I.R. IRAN

Taeb, Abbas*⁺

Department of Chemistry Engineering, Iran University of Science and Technology,
P.O. Box 16846-13114 Tehran, I.R. IRAN

ABSTRACT: *In the present study, the applicability of a bimetallic Pt-Sn/Al₂O₃ in propane dehydrogenation with different promoters, namely, Ca, Mg, and incorporation of Mg-K and Ca-K was studied. The catalysts were prepared by the sequential impregnation of γ -alumina support and characterized by TPD, SEM, XRD, and UV analysis. The propane conversion and propylene selectivity were evaluated under representative industrial conditions. The results showed that the Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst had a better performance in terms of propane conversion and propylene selectivity and yield, due to the partially neutralized and synergistic effect of Mg and K (probably by increasing the platinum dispersion and preventing side reaction and coke formation). TPD results also showed the effects of all these promoters (Ca, Mg, Ca-K and Mg-K) on the reduction of acidic sites of the catalyst, which are favorable sites for cracking reaction and coke formation. In the meantime, Ca is more effective in reducing strong acidic sites, but also Mg is more effective in reducing weak and medium-strength acid sites. Therefore, alkaline-earth metals and also using them with potassium could reduce side reaction products and lead to a more selective reaction to propylene, and improve catalyst performance compared to industrial catalysts.*

KEYWORDS: *Propane Dehydrogenation; Alkaline-Earth Metals; Promoter; Catalyst Performance.*

INTRODUCTION

Fossil fuels, especially alkanes are still the most important source of energy in the world [1]. Nevertheless the world's demand for products derived from alkanes

such as propylene by the chemical industry for a variety of polymers and intermediates in the chemical industry has been growing as a feedstock [2,3]. Currently, the main

* To whom correspondence should be addressed.

+ E-mail: taeb@iust.ac.ir

1021-9986/2022/6/1921-1931

11/\$/6.01

source for propylene is from the by-production of gasoline from thermal/catalytic cracking [4]. The propane dehydrogenation process to propene not only has great potential as a propylene booster but also reduced the gap between the supply and demand for propylene [5,6].



It has been shown that propane dehydrogenation is assumed as the following reaction rate:

$$-r = k' C_{\text{propane}} - k'' C_{\text{propylene}} \quad (2)$$

$$C_{\text{H}_2} = k' \left(C_{\text{propane}} - \frac{C_{\text{propylene}} C_{\text{H}_2}}{K_{\text{eq}}} \right)$$

where r is the rate of conversion of propane to propylene per catalyst weight, k' and k'' are the rate constants of forwarding and backward reactions, respectively, C is the concentration and K_{eq} is the equilibrium constant [7]. *Farjo et al.* described the kinetic of the propane dehydrogenation in terms of a Langmuir–Hinshelwood mechanism and reported the adsorption of propane was the rate-controlling step [8].

Despite the simple chemistry, propane dehydrogenation under industrial reaction conditions is very complex with side reactions such as deep dehydrogenation, polymerization, coke formation, hydrogenolysis, and cracking; which lead to more reaction complexity and operating costs and less product purity [9]. Dehydrogenation of propane is an endothermic reaction in which relatively high reaction temperatures (773–873 K) and low pressures (0.3–1 atm) are industrially used to obtain commercially acceptable conversions and good propylene yield [10,11]. Also, it should be noted that an equal chance of reacting for all of the equivalent C–H bonds in propane lead to a nonselective dehydrogenation reaction [10]. Furthermore, the high operating temperatures promote thermal cracking reactions to form coke and light alkanes, which leads to decreased propylene yield and increased catalyst deactivation [11,12]. Therefore, in order to achieve higher propane conversion, higher yield, and selectivity to propylene, the reaction should be controlled by catalyst formulation.

Since the acidity of catalysts is a very important factor in catalyst stability and performance. Also, the addition of alkali and alkaline-earth metals promoters to Pt-Sn/Al₂O₃ dehydrogenation catalyst can suppress acid-catalyzed side

reactions such as cracking, isomerization, and polymerization *via* neutralizing the acidic sites of the support, finally improving the stability and performance of catalysts [13,14]. Thus, it is of great significance to develop catalysts for propane dehydrogenation with low acidic sites and low side reaction products which lead to high stability and performance of catalysts.

Platinum-based mono- and bimetallic (Pt-Sn) catalysts supported on γ -Al₂O₃ have been widely used in hydrocarbon dehydrogenation, but bimetallic platinum-tin catalysts showed higher reaction conversion and selectivity [5,15,16]. The stability and selectivity of the paraffin dehydrogenation process for the production of olefins increase by suppressing the cracking process, isomerization reactions, and the coke formation process [2,4,17]. Over the past several years, attention has been focused on Pt-Sn catalysts, and significant progress has been made in their development [15,18,19]. The properties of bimetallic Pt-Sn catalysts strongly depend on the interaction between Pt and Sn, as well as the state of Sn [16,17,20].

Sn can modify the electronic and geometric properties of Pt. For example; Sn decreases the size of Pt ensembles and reduces hydrogenolysis and coking reactions that require large Pt ensembles [21]. The electronic modification of Sn on Pt consists of the positive charge transfer from Snⁿ⁺ species and different electronic structures of PtSn alloys [19,22,23].

Tasbihi et al. [18] found that the additions of K and Li to Pt-Sn/ γ -Al₂O₃ catalyst resulted in significantly higher catalytic performance compared to the Pt-Sn/ γ -Al₂O₃ catalyst. Nagaraja and coworkers [24] reported that the addition of a small amount of K to the bimetallic PtSn/ γ -Al₂O₃ catalyst improved the n-C₄ yield. The addition of potassium blocked the acid sites of Pt catalyst and improved the selectivity of Pt-Sn/ γ -Al₂O₃ catalyst. *Siri et al.* [21] reported that K addition to the catalyst improved the stability level of the catalyst in the dehydrogenation reaction. However, the dehydrogenation performance of Pt-Sn catalysts is still not satisfactory, especially concerning the stability of the catalysts. Therefore, it is necessary to improve the stability of Pt-Sn catalysts in light paraffin conversion.

Alipour et al. [25] found that a certain amount of alkaline-earth metal oxide (MgO and CaO) could increase the catalytic performance of Ni/Al₂O₃ and Ni/SiO₂ because of the strong interaction between Ni and the support. The effect of alkaline earth metals over

Ru-based catalysts were investigated by *Li et al.* [26]. They showed that the addition of K, Mg, and Ca significantly enhanced the catalysis activities. The effects of alkaline-earth metals on Fe/SiO₂ catalysts were described by *Li et al.* [27]. They found that the alkaline-earth metals strengthened Fe-O bonds of Fe₂O₃ in prepared catalysts. Yu and coworkers [28] investigated the performance of a Ca-doped Pt/ γ -Al₂O₃ catalyst for cyclohexane dehydrogenation with different amounts of Ca and different impregnation orders. They reported, that the addition of Ca significantly improved the performance of Pt/Al catalyst. As well, the influence of Mg addition on PtSnK/ γ -Al₂O₃ catalyst for isobutene dehydrogenation was studied by *Zhang et al.*. They found that the Pt dispersion increased and the carbon depositions decreased with suitable amounts of Mg [16]. Regarding the effects of Mg, Ca, and K on the performance of dehydrogenation catalyst, we expect using Mg with K and Ca with K to show better performance to use each of these promoters alone on Pt-Sn/ γ -Al₂O₃ catalyst for propane dehydrogenation. Thus, in the present study, we investigated the effects of alkaline-earth metals (Mg and Ca) and the mixed effect of alkali and alkaline-earth metals (Mg-K and Ca-K) as promoters on Pt-Sn/ γ -Al₂O₃ catalyst for reducing acidic sites of catalysts and improving catalytic performance in the dehydrogenation of propane. The catalysts were studied by XRD, TPD, SEM, and UV analysis techniques.

EXPERIMENTAL SECTION

Catalysts Preparation

Materials

The spherical γ -Al₂O₃ support ($S_{\text{BET}}=215\text{m}^2/\text{g}$ with total pore volume (0.531 m³/g)) was purchased from Axen Co. The precursors of impregnation were H₂PtCl₆.6H₂O (40%) was purchased from Merck, SnCl₂.H₂O (97%) was purchased from Janssen and pure Ca(NO₃)₂.6H₂O, Mg(NO₃)₂.6H₂O and KNO₃.6H₂O were purchased from Merck. HCl (37%) and HNO₃ (65%) were purchased from Merck. All solutions were prepared with distilled water.

Methods

The catalyst samples were prepared by a sequential impregnation of the precursors. A commercial γ -Al₂O₃ was used as a support, which was previously calcined in air at 550 °C for 2 h. The support was wetness impregnated first with using the hydrochloric acid solution of SnCl₂,

then with using a hydrochloric acid solution of H₂PtCl₆, and finally dried impregnated with using a nitric acid solution of Ca(NO₃)₂, Mg(NO₃)₂ and KNO₃. After impregnation, the samples were dried at 120°C overnight and calcinated in the air at 550°C for 2 h at a rate of 5 °C/min. Mg (0.65 wt.%), Ca (0.65 wt.%), Mg-K (0.65 wt.%), and Ca-K (0.65 wt.%) loaded in each of the four catalysts, and the contents of Pt and Sn were fixed at 0.5 and 0.71 wt.% for all catalysts. The industrial Pt-Sn/ γ -Al₂O₃ catalyst (PD-IND) [29], was selected as a performance reference.

Characterization methods

XRD

The X-Ray Diffraction (XRD) patterns of support were performed by using a Philips Expert PW 2404 with a copper anode ($\lambda=1.54439$ and 1.54056 Å). Phases were recognized through a comparison with JCPDS files.

TPD

The acidity of samples was measured by temperature-programmed desorption of ammonia (TPD-NH₃) using a BELCAT-A analyzer. Prior to the adsorption of ammonia, each sample was heated under a helium stream (50 ml/min) from room temperature up to 500 °C. Subsequently, the sample was cooled down and saturated in a flow of ammonia (2.5 mL/min) at 100 °C for 1 h. The ammonia desorbed during the temperature rise from 100 °C to 600 °C with a heating rate of 10 °C/min was analyzed by a thermal conductivity detector.

SEM

The uniformity of the layer deposited by impregnation on the catalyst was carried out using Scanning Electronic Microscope (VEGA\TESCAN analyzer). Prior to the examination, samples were placed on aluminum stubs and coated with gold under an argon atmosphere. An EDAX CDU LEAP X-ray detector was used for the measurement of the wavelength and Pt adsorption.

UV-Vis spectroscopy

The platinum concentration within the solution container was recorded by using Metrohm 744 UV-Vis spectrometer before and after Pt impregnation.

The performance test

The performance test of both synthesized and

commercial catalysts were conducted in a fixed bed quartz reactor (ID=15 mm) using a mixture of hydrogen and propane (for dilution of propane in a gas mixture to increase propane conversion). Catalyst particles (2 g) diluted with 4 cc quartz sand were packed in the reactor. The catalyst was reduced in hydrogen flow at 530 °C for 1 h in the reactor. Attempts have been made to close the test conditions to industrial operating conditions ($H_2/CH_4:0.85$; $WHSV=2(1/h)$ and $T=620^\circ C$) under atmospheric pressure. The product was analyzed for light hydrocarbons using Agilent 6890N Gas Chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and two Flame Ionization Detectors (FID). Propane conversion and selectivity and yield to products were calculated as [30]:

$$\text{Propane conversion (mol \%)} = \frac{\text{moles of propane reacted}}{\text{moles of propane fed}} \times 100$$

$$\text{Selectivity to species } i \text{ (mol\%)} = \frac{\text{moles of product } i \text{ formed}}{\text{moles of propane reacted}} \times \left(\frac{N_i}{N_{\text{propane}}}\right) \times 100$$

$$\text{Yield to species } i \text{ (mol\%)} = \frac{\text{moles of product } i \text{ formed}}{\text{moles of propane fed}} \times 100$$

Where i refers to reaction products including propylene, ethylene, ethane, and methane; and N_i and N_{propane} refer to the number of carbon atoms per molecule in the product and propane, respectively.

RESULTS AND DISCUSSION

Characterization of the catalysts

XRD analysis

X-Ray diffraction pattern of support as detected by the X-ray diffraction test is presented in Fig. 1. As can be seen, typical peaks of support at 37° , 46° , and 67° were recorded, which confirms the amorphous structure and also γ phase of support. Due to the low weight percentage of promoters used in these catalysts, changing γ phase of support seems unlikely and these promoters just absorbed support with no significant change in support.

TPD analysis

The effects of alkaline earth metals as promoters on the acidity of Pt-Sn/ γ - Al_2O_3 catalysts were determined by NH_3 -TPD experiments. A comparison of the desorption peaks was obtained with the deconvolution of peaks by computing the normal distribution function. As can be seen in Fig. 2, there are three desorption peaks. The low-temperature peak which occurs at about 170-190°C,

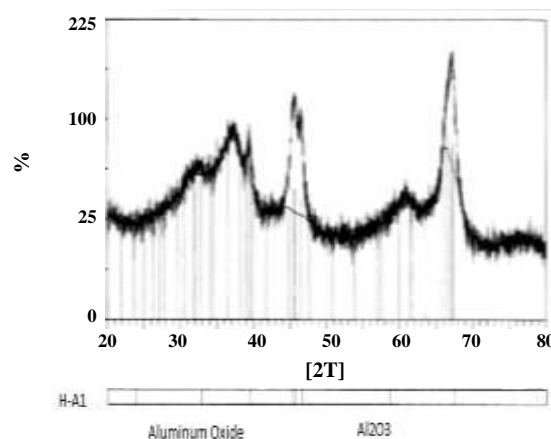


Fig. 1: XRD patterns of support of catalyst.

was to weak acid sites and the peak that occurs at about 230-290 °C was attributed to medium-strength acid sites. As well as, the peak of higher temperatures than 290 °C was related to the strong acid sites. The desorption peak, total acidity, and acidity strength amount for catalysts with alkaline earth metals and PD-IND catalysts are shown in Table 1.

Fig. 2 shows that the lowest total acidity amount (1.088 mmol NH_3/g_{cat}) is related to Pt-Sn-Ca-K/ γ - Al_2O_3 , furthermore, it has been shown that the lowest acidity amount of strong acid sites is also related to Pt-Sn-Ca-K/ γ - Al_2O_3 , that means this catalyst could reduce more strong acid sites compared to other catalysts and the effect of this catalyst on neutralization of strong acid sites is more than on neutralization of medium and weak acid sites. Similar results were obtained by Yu *et al.* [28] for the effect of Ca on the reduction of strong acid sites. It was also reported that Ca can reduce the acidity of γ - Al_2O_3 by anchoring onto the Al^{3+} acid sites. In addition, the competing adsorption of Ca with $[PtCl_6]^{2-}$ in the impregnation procedure is another proposed possible reason for the inhibition effects of Ca on the formation of acid sites [28].

The effect of Mg on the catalyst performance was specified by comparing the acidity of Pt-Sn-Ca-K/ γ - Al_2O_3 (1.088 mmol NH_3/g_{cat}) with Pt-Sn-Mg-K/ γ - Al_2O_3 (1.235 mmol NH_3/g_{cat}) and also Pt-Sn-Ca/ γ - Al_2O_3 (1.325 mmol NH_3/g_{cat}) with Pt-Sn-Mg/ γ - Al_2O_3 (1.289 mmol NH_3/g_{cat}) catalysts. Interestingly, the NH_3 -TPD profile of Pt-Sn-Mg-K/ γ - Al_2O_3 and Pt-Sn-Mg/ γ - Al_2O_3 shows that weak acid sites are reduced. As shown in Table 1, weak acid sites totally vanished for Pt-Sn-Mg-K/ γ - Al_2O_3 , but for Pt-Sn-Mg/ γ - Al_2O_3 is the part of the weakly acidic sites

Table 1: TPD results: Desorption peak, total acidity and acidity strength amount of catalysts.

catalyst	weak acid sites		medium strength acid sites		strong acid sites		Total acidity amount mmol NH ₃ /g _{cat}
	desorption peak °C	acidity amount mmol NH ₃ /g _{cat}	desorption peak °C	acidity amount mmol NH ₃ /g _{cat}	desorption peak °C	acidity amount mmol NH ₃ /g _{cat}	
Pt-Sn-Ca/ γ -Al ₂ O ₃	169	0.188	256	0.364	672	0.77	1.325
Pt-Sn-Mg/ γ -Al ₂ O ₃	-	-	195	0.415	617	0.874	1.289
Pt-Sn-Ca-K/ γ -Al ₂ O ₃	185	0.161	287	0.466	703	0.466	1.088
Pt-Sn-Mg-K/ γ -Al ₂ O ₃	-	-	239	0.514	710	0.721	1.235
PD-IND	408	-	659	-	839	-	11.66

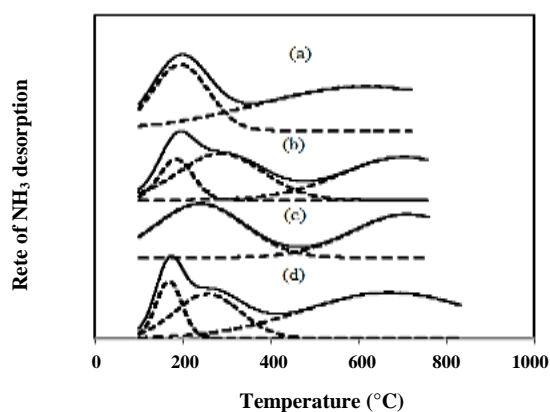


Fig. 2: NH₃-TPD profiles of the samples. (a): Pt-Sn-Mg/ γ -Al₂O₃, (b): Pt-Sn-Ca-K/ γ -Al₂O₃, and (c): Pt-Sn-Mg-K/ γ -Al₂O₃ (d): Pt-Sn-Ca/ γ -Al₂O₃.

and part of the medium-strength acidic sites was poisoned by adsorbed Mg, accordingly, the second adsorption peak appeared at a lower temperature (195°C). These results also showed the effect of Mg on the suppression of acidic sites to avoid side reactions on acid sites. The results of Table 1 showed that the presence of K with Ca and Mg increased the desorption peak, which might be due to less potassium effect on decreasing the number of acidic sites compared to Mg and Ca.

All catalysts compared to industrial catalysts (PD-IND) showed better results both in terms of reducing total acidity (PD-IND : 11.66 mmol NH₃/g_{cat}) and desorption peak (PD-IND : 408, 659, and 839 °C). Therefore synthesized catalysts could reduce the acidity of the Pt-Sn/Al systems, which led to reducing the adsorption of propylene and undesired products of side reactions, thus improving catalytic stability.

SEM analysis

The catalyst particle size and uniformity of Pt-Sn-Mg-

K/ γ -Al₂O₃ deposited on γ -Al₂O₃ spheres were investigated by Scanning Electronic Microscope (SEM). Fig. 3 shows two photographs of a calcined sample, which shows that the catalyst was generally uniformly dispersed. The SEM results are also shown in Table 2, which determined the contents of Pt deposited on the aged, center, and center-middle-edge catalyst. Table 2 indicated the non-uniform distribution of Pt on the Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst. Approximately, There was no detected Pt on the edge and middle of the catalyst, while a large amount of Pt was accumulated in the center of the catalyst, which was similar to the ovoid core arrangement. Therefore, access to the active phase by the reactant would be difficult, and consequently, the possibility of forming side reactions increased.

UV analysis

The initial Pt concentration on the impregnation solvent before impregnation and the final Pt concentration after impregnation was recorded by using UV-Vis spectrometer as shown in Table 3. As it can be seen Pt-Sn-Mg/ γ -Al₂O₃ adsorbed the lowest percentage of platinum (89.45%) in the impregnation solution, compared to other catalysts. UV results also showed that the percentage of Pt adsorption for all catalysts is acceptable value, which means all promoters could be effective for Pt adsorption on catalysts.

Performance results

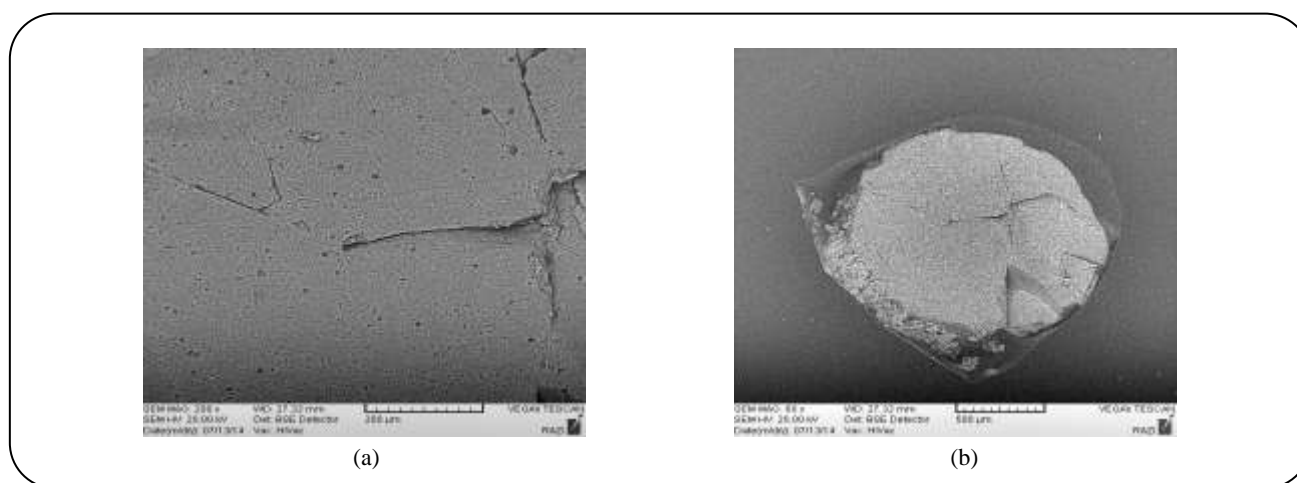
The catalyst performances, in terms of propane conversion, propylene selectivity, and propylene yield are shown in Figs. 4, 5, and 6, respectively. Fig. 3 shows that all catalysts indicated conversion decay during reaction time, which was the result of the catalysts' deactivation. Generally, the deactivation rates regarding side reactions are reported as first-order and independent of reaction [13]:

Table 2: The results of SEM analysis.

	Center (Wt.%)	Edge (Wt.%)	Middle (Wt.%)
Pt	0.4	0.01	0.01

Table 3: The results of UV-analysis.

Run no.	Solution specification	Initial Pt concentration (mmol/lit)	Final Pt concentration (mmol/lit)	Percent of adsorption (%)
1	Pt-Sn-Ca/ γ -Al ₂ O ₃	7.02	0.449	93.60
2	Pt-Sn-Ca-K/ γ -Al ₂ O ₃	7.02	0.449	93.60
3	Pt-Sn-Mg/ γ -Al ₂ O ₃	7.02	0.74	89.45
4	Pt-Sn-Mg-K/ γ -Al ₂ O ₃	7.02	0.449	93.60

**Fig. 3 SEM image of the Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst. (a): Top view and (b): sectional view.**

$$-\frac{da}{dt} = k_d a \quad (3)$$

Where a is catalyst activity and k_d is the respective rate constant of deactivation. Equation (2) shows that Catalyst deactivation increases with reaction time due to coke formation, that's the reason for the reduction of catalyst conversion with the reaction time in performance results of catalysts [7,13].

As can be seen in Figs. 4-6, The Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst showed the highest propane conversion, propylene selectivity, and propylene yield than other catalysts. While Pt-Sn-Mg/ γ -Al₂O₃ catalyst showed less propane conversion and propylene selectivity and yield that Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst. It means the synergistic effect between Mg and K led to better performance of Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst.

The role of magnesium in dehydrogenation catalysts has been reported that Mg could promote the reduction

of Pt and increase the metal dispersion [16]. Mg was also neutralizing the acidity of support [16]. On the other hand, there are two types of active Pt species (Pt1 sites and Pt2 sites) on the surface of the supported platinum catalyst. Pt1 is the site in which Pt directly anchors on the carrier surface, while Pt2 corresponds to the site in which Pt anchors on tin oxide's surface with a "sandwich structure". The Pt1 sites are mainly responsible for the hydrogenolysis reaction and carbon deposits and the Pt2 sites are the main reaction active sites for the dehydrogenation of propane [31]. Zhang *et al.* reported that the appropriate amount of Mg could increase the platinum dispersion and stabilize the oxidation states of Sn species, which was favorable to the formation of the Pt2 sites and responsible for the improvement of the catalytic activity [16]. Also, the synergistic effect between potassium and tin was described by Zhang [15]. This synergistic effect might lead to an easier movement of the deposited carbon from the metal to the support

and could also, prevent coke formation that covered the active metal [24]. Therefore; the synergistic effect between Mg, K and Sn can be responsible for the high performance of Pt-Sn-Mg-K/ γ -Al₂O₃.

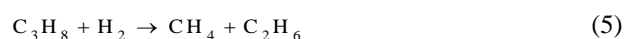
Figs. 4 and 5 show that Pt-Sn-Ca-K/ γ -Al₂O₃ has second place after Pt-Sn-Mg-K/ γ -Al₂O₃ in terms of conversion and selectivity. Ca could reduce the interaction between metal and support by competing with active metal to support interaction [28, 32] by forming a sandwich construction that largely reduces the Pt-Al interface [29]. Ca also modify the adsorption performance of active metal on the supports [33]. These effects might be responsible for improving the effects of Ca on Pt-Sn-Ca-K/ γ -Al₂O₃ performance.

Less conversion decline can be seen on Pt-Sn-Ca-K/ γ -Al₂O₃ and Pt-Sn-Mg-K/ γ -Al₂O₃ catalysts compared to Pt-Sn-Ca/ γ -Al₂O₃ and Pt-Sn-Mg/ γ -Al₂O₃ catalysts. This might be due to the effects of using K with Mg and Ca. The incorporation of Mg-K and Ca-K might strengthen the interaction between the metal phase and support due to the higher stability of the metal phase and preventing the formation of coke precursors is the main reason for the dramatic decrease of catalytic activity. Thus, the activity decline for Pt-Sn-Mg-K/ γ -Al₂O₃ and Pt-Sn-Ca-K/ γ -Al₂O₃ are lower than Pt-Sn-Mg/ γ -Al₂O₃ and Pt-Sn-Ca/ γ -Al₂O₃, respectively. Also, as can be seen in Figs. 5-6, better propylene selectivity and yield were observed for Pt-Sn-Mg-K/ γ -Al₂O₃ and Pt-Sn-Ca-K/ γ -Al₂O₃ catalysts and the difference in selectivity and yield of Pt-Sn-Mg/ γ -Al₂O₃ and Pt-Sn-Ca/ γ -Al₂O₃ catalysts is not noticeable. In general, Mg represented better performance than Ca in terms of propane conversion and propylene selectivity, and yield. This might be due to the Mg effect on neutralizing weak acid sites that were identified by the TPD test.

Fig. 6 shows that all synthesized catalysts have shown better performance than PD-IND catalysts, due to the reduction of acidic sites of catalyst that was proven by TPD analysis. These results indicate our study could introduce synthesized catalysts with better catalytic performance than a current industrial catalyst for dehydrogenation of propane, which reduces the cost of propylene production.

Side reaction products

Furthermore, the main reaction of propane dehydrogenation following side reactions occur:



$$\Delta H_{298}^\circ = -63.4 \text{ kJ / mol}$$

Reaction (3) is the cracking of propane to methane and ethylene on Pt-Sn catalyst, which takes place both in the gas phase (thermal conversion) and also on the surface of the catalyst (catalytic conversion). Hydrogenolysis (4) as a catalytic side reaction also occurs on the surface of Pt-Sn catalysts. Therefore, the main side reaction products involve methane, ethylene, and ethane [8].

The cracking and hydrogenolysis rate can be assumed to be first order as following rate equations [8]:

$$\text{Thermal cracking} \quad r = k_1 P_{\text{C}_3\text{H}_8} \quad (6)$$

$$\text{Catalytic cracking} \quad r = k_2 P_{\text{C}_3\text{H}_8} \quad (7)$$

$$\text{hydrogenolysis} \quad r = k_3 P_{\text{C}_3\text{H}_8} P_{\text{H}_2} \quad (8)$$

Where $P_{\text{C}_3\text{H}_8}$ and P_{H_2} are the partial pressures of propane and hydrogen and k is the rate constant which is proposed as follows [8]:

$$k_1 = 1.53 \text{E} + 09 \exp\left(\frac{-1598.23}{T}\right) \quad (9)$$

$$k_2 = 1.14 \exp\left(\frac{-6488}{T}\right) \quad (10)$$

$$k_3 = 1.34 \times 10^7 \exp\left(\frac{-27393}{T}\right) \quad (11)$$

Where T is the reaction temperature.

On the other hand, coke formation results in catalyst deactivation during propane dehydrogenation is a well-known phenomenon [34]. Coke formation on the catalyst occurs from several routes, such as deep cracking of propane, deep dehydrogenation, propene polymerization, and condensation of large molecules [35]. Therefore, the reduction of side reaction products leads to a reduction of coke formation and catalyst deactivation during propane dehydrogenation. A coking reaction occurs both on the surface of the metal and the support of the catalyst. The coking rate on the fresh catalyst is assumed as follows [34]:

$$r_c = k_c P_{\text{C}_3\text{H}_8}^2 / (1 + k_4 P_{\text{C}_3\text{H}_8})^4 \quad (12)$$

Where r_c is the rate of coking reaction, k_c is the coking reaction rate constant and k_4 is the adsorption equilibrium constant were estimated to be $4.15 \times 10^{-5} \text{ mg}_{\text{coke}}/\text{mg}_{\text{catalyst}}$ and 7.18×10^{-1} , respectively, by *Li et al.* [36].

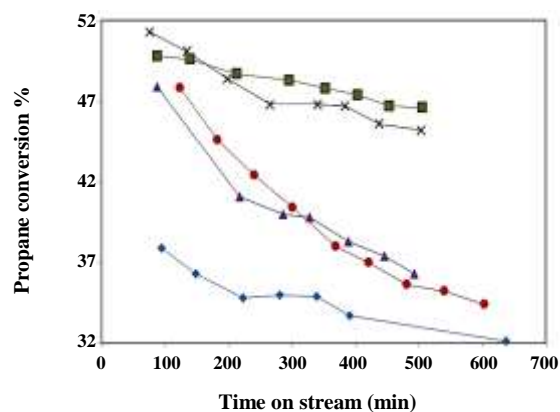


Fig. 4: Comparison of propane conversion for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 h⁻¹; T=620 °C; H₂/CH: 0.85).

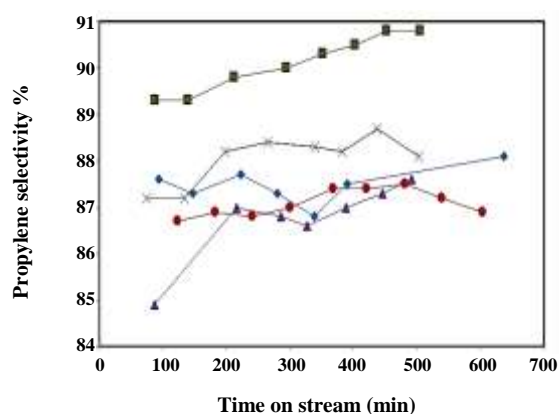


Fig. 5: Comparison of propylene selectivity for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 (1/h); T=620 °C; H₂/CH: 0.85).

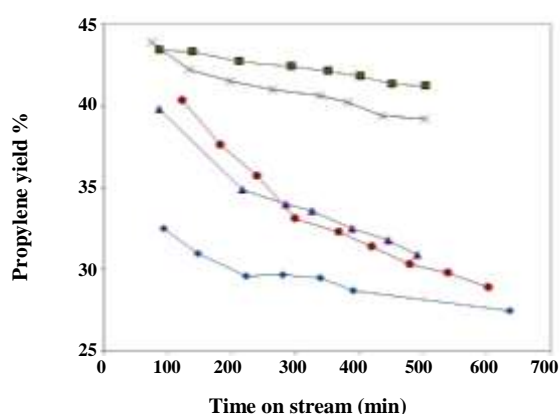


Fig. 6: Comparison of propylene yield for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 (1/h); T=620 °C; H₂/CH: 0.85).

It can be seen in Fig. 4 that all catalysts showed conversion decay during time-on-stream, thereby indicating that the catalyst deactivation was probably due to coke deposits. Acidic sites in the support of dehydrogenation catalysts can promote cracking and coke formation reactions [7]. Therefore neutralization of these sites by alkaline-earth metals as promoters can reduce cracking and coke production. To study the effects of alkaline-earth metals on side reactions productions, the selectivity of methane, ethylene and ethane for synthesized and industrial catalysts was calculated and shown in Figs. 7-9, respectively. As can be seen in Figs. 7 and 8 the selectivity of CH₄ and C₂H₄ as main cracking products for Pt-Sn-Mg-K/ γ -Al₂O₃ catalyst is lowest than other catalysts. This means the synergistic effect between Mg and K led to a reducing cracking reaction and consequently coke formation. Fig. 9 also shows that the selectivity of ethane as a hydrogenolysis reaction product on Pt-Sn-Ca/ γ -Al₂O₃ and Pt-Sn-Ca-K/ γ -Al₂O₃ is higher than other catalysts, which means Ca less than Mg could be able to reduce hydrogenolysis reaction, that might be one of the reasons for better performance of catalysts with Mg promoter compared to Ca promoter.

CONCLUSIONS

A comparison of Mg, Ca, Mg-K and Ca-K as promoters showed that Mg exhibited better superior promoting effects than Ca on the Pt-Sn/ γ -Al₂O₃ catalyst in the dehydrogenation of propane. Among synthesized catalysts, Pt-Sn-Mg-K/ γ -Al₂O₃ showed the highest propane dehydrogenation performance due to the synergistic effect between Mg and K, which led to producing fewer side reaction products and consequently coke formation. This synergistic effect also could overcome the effect of Pt accumulation in the catalyst center with the possible effect of Mg on the formation of Pt₂ sites and promotion of Pt reduction on dehydrogenation catalyst. All synthesized catalysts showed better catalytic performance compared to PD-IND catalysts, due to the reduction of catalyst acidity proven by TPD results, and consequently reduction of side reaction products.

Acknowledgements

The authors would like to thank Petrochemical Research and Technology Company (NPC-RT) for the financial support of this work.

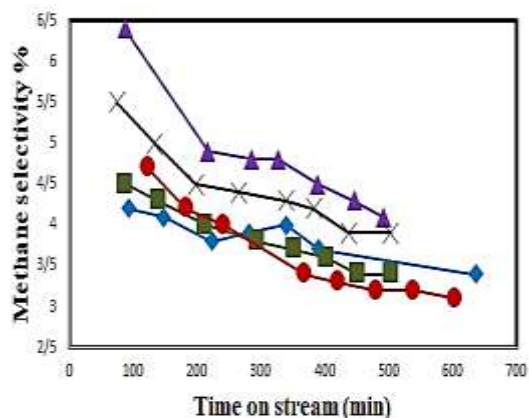


Fig. 7: Comparison of methane selectivity for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 (1/h); T=620 °C; H₂/CH₄: 0.85).

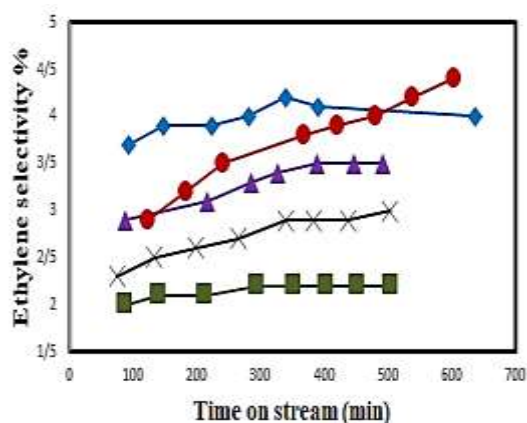


Fig. 8: Comparison of ethylene selectivity for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 (1/h); T=620 °C; H₂/CH₄: 0.85).

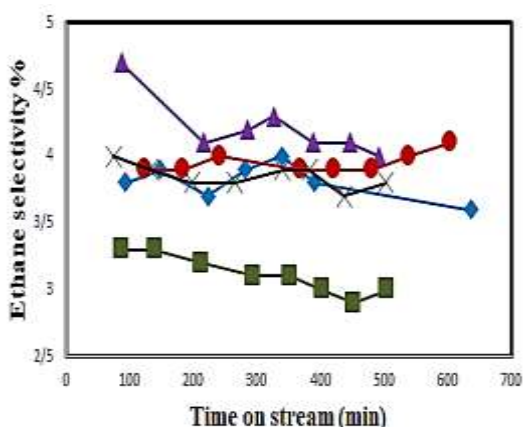


Fig. 9: Comparison of ethane selectivity for Pt-Sn-Ca (▲), Pt-Sn-Ca-K (×), Pt-Sn-Mg (●), Pt-Sn-Mg-K (■), and PD-IND (◆) on γ -alumina supports (WHSV=2 (1/h); T=620 °C; H₂/CH₄: 0.85).

Received : Aug. 5, 2021 ; Accepted : Nov. 1, 2021

REFERENCES

- [1] Rasaei Y., Towfighi Darian J., Royaei S.J., Experimental Investigation and Kinetic Modeling of Naphtha Catalytic Reforming Using Pt-Re/Al₂O₃ Catalyst, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **40**(1): 275-287 (2021).
- [2] Pisduangdaw S., Panpranot J., Chaisuk C., Faungnawakij K., Mekasuwandumrong O., Flame Sprayed Tri-Metallic Pt-Sn-X/Al₂O₃ Catalysts (X= Ce, Zn, and K) for Propane Dehydration, *Catal. Commun.*, **12**(12):1161-1165 (2011).
- [3] Zhang Y., Zhou Y., Shi J., Zhou S., Zhang Z., Zhang S., Guo M., Propane Dehydrogenation Over PtSnNa/La-doped Al₂O₃ Catalyst: Effect of La Content. *Fuel Processing Technology*, *Fuel Process. Technol.*, **111**: 94-104 (2013).
- [4] Yu C., Ge Q., Xu H., Li W., Effects of Ce Addition on the Pt-Sn/ γ -Al₂O₃ Catalyst for Propane Dehydrogenation to Propylene, *Appl. Catal. A*, **315**: 58-67 (2006).
- [5] Wang Y., Wang Y., Wang S., Guo X., Zhang S.M., Huang W.P., Wu S., Propane Dehydrogenation over PtSn Catalysts Supported on ZnO-Modified MgAl₂O₄, *Catal. Lett.*, **132**(3-4): 472 (2009).
- [6] Wu Z., Hatim I.M., Kingsbury B.F., Gbenedio E., Li K., A Novel Inorganic Hollow Fiber Membrane Reactor for Catalytic Dehydrogenation of Propane, *AIChE J.*, **55**(9): 2389-2398 (2009).
- [7] Sahebdehfar S., Ravanchi M.T., Zangeneh F.T., Mehrzama S., Rajabi S., Kinetic Study of Propane Dehydrogenation and Side Reactions over Pt-Sn/Al₂O₃ Catalyst, *Chem. Eng. Res. Des.*, **90**(8): 1090-1097 (2012).
- [8] Farjoo A., Khorasheh F., Niknaddaf S., Soltani M., Kinetic Modeling of Side Reactions in Propane Dehydrogenation Over Pt-Sn/ γ -Al₂O₃ Catalyst, *Sci. Iran.*, **18**(3): 458-464 (2011).
- [9] Sahebdehfar S., Tahiri Z.F., Dehydrogenation of Propane to Propylene over Pt-Sn/Al₂O₃ Catalysts: the Influence of Operating Conditions on Product Selectivity, *Iran. J. Chem. Eng. (IJChE)*, **7**(2): 51-57 (2010).
- [10] Michorczyk P., Ogonowski J., Dehydrogenation of Propane to Propene over Gallium Oxide in the Presence of CO₂, *Appl. Catal. A Gen.*, **251**(2): 425-433 (2003).

- [11] Xu B., Zheng B., Hua W., Yue Y., Gao Z., [Support Effect in Dehydrogenation of Propane in the Presence of CO₂ over Supported Gallium Oxide Catalysts](#), *J. Catal.*, **239**(2): 470-477 (2006).
- [12] Zheng B., Hua W., Yue Y., Gao Z., [Dehydrogenation of Propane to Propene over Different Polymorphs of Gallium Oxide](#), *J. Catal.*, **232**(1): 143-151 (2005).
- [13] Tahriri Z.F., Taeb A., Gholivand K., Sahebdehfar S., [The Effect of Alkali Metal Promoters on the Stability and Coke Formation of Platinum-Based Propane Dehydrogenation Catalysts: A Kinetic Study](#), *Iran. J. Chem. Chem. Eng. (IJCCCE)*, **32**(4): 25-32 (2013).
- [14] Vu B.K., Song M.B., Ahn I.Y., Suh Y.W., Suh D.J., Kim J.S., Shin E.W., [Location and Structure of Coke Generated over Pt-Sn/Al₂O₃ in Propane Dehydrogenation](#), *J. Ind. Eng. Chem.*, **17**(1): 71-76 (2011).
- [15] Zhang Y., Zhou Y., Wan L., Xue M., Duan Y., Liu X., [Synergistic Effect Between Sn and K Promoters on Supported Platinum Catalyst for Isobutane Dehydrogenation](#), *J. Nat. Gas Chem.*, **20**(6): 639-646 (2011).
- [16] Zhang Y., Zhou Y., Wan L., Xue M., Duan Y., Liu X., [Effect of Magnesium Addition on Catalytic Performance of PtSnK/ \$\gamma\$ -Al₂O₃ Catalyst for Isobutane Dehydrogenation](#), *Fuel Process. Technol.*, **92**(8): 1632-1638 (2011).
- [17] Tasbihi M., Feyzi F., Amlashi M.A., Abdullah A.Z., Mohamed A.R., [Effect of the Addition of Potassium and Lithium in Pt-Sn/Al₂O₃ Catalysts for the Dehydrogenation of Isobutane](#), *Fuel Process. Technol.*, **88**(9): 883-889 (2007).
- [18] He S.B., Bi W.J., Lai Y.L., Xing R., Xu Y., Sun C.L., [Effect of Sn Promoter on the Performance of Pt-Sn/ \$\gamma\$ -Al₂O₃ Catalysts for n-Dodecane Dehydrogenation](#), *J. Fuel Chem. Technol.*, **38**(4): 452-457 (2010).
- [19] Lee M.H., Nagaraja B.M., Lee K.Y., Jung K.D., [Dehydrogenation of Alkane to Light Olefin Over PtSn/ \$\theta\$ -Al₂O₃ Catalyst: Effects of Sn Loading](#), *Catal. Today*, **232**: 53-62 (2014).
- [20] Zhang Y., Zhou Y., Shi J., Sheng X., Duan Y., Zhou S., Zhang Z., [Effect of Zinc Addition on Catalytic Properties of PtSnK/ \$\gamma\$ -Al₂O₃ Catalyst for Isobutane Dehydrogenation](#), *Fuel Process. Technol.*, **96**: 220-227 (2012).
- [21] Siri G.J., Bertolini G.R., Casella M.L., Ferretti O.A., [PtSn/ \$\gamma\$ -Al₂O₃ Isobutane Dehydrogenation Catalysts: the Effect of Alkali Metals Addition](#), *Mater. Lett.*, **59**(18): 2319-2324 (2005).
- [22] Armendariz H., Guzman A., Toledo J.A., Llanos M.E., Vazquez A., Aguilar-Rios G., [Isopentane Dehydrogenation on Pt-Sn Catalysts Supported on Al-Mg-O Mixed Oxides: Effect of Al/Mg Atomic Ratio](#), *Appl. Catal. A*, **211**(1): 69-80 (2001).
- [23] Yu C., Xu H., Ge Q., Li W., [Properties of the Metallic Phase of Zinc-Doped Platinum Catalysts for Propane Dehydrogenation](#), *J. Mol. Catal. A*, **266**(1-2): 80-87 (2007).
- [24] Nagaraja B.M., Jung H., Yang D.R., Jung K.D., [Effect of Potassium Addition on Bimetallic PtSn Supported \$\theta\$ -Al₂O₃ Catalyst for n-Butane Dehydrogenation to Olefins](#), *Catal. Today*, **232**: 40-52 (2014).
- [25] Alipour Z., Rezaei M., Meshkani F., [Effect of Alkaline Earth Promoters \(MgO, CaO, and BaO\) on the Activity and Coke Formation of Ni Catalysts Supported on Nanocrystalline Al₂O₃ in Dry Reforming of Methane](#), *J. Ind. Eng. Chem.*, **20**(5): 2858-2863 (2014).
- [26] Li H., Ji D., Li Y., Liang Y., Li G.X., [Effect of Alkaline Earth Metals on the Liquid-Phase Hydrogenation of Hydroquinone over Ru-Based Catalysts](#), *Solid State Sci.*, **50**: 85-90 (2015).
- [27] Li J., Zhang C., Cheng X., Qing M., Xu J., Wu B., Yang Y., Li Y., [Effects of Alkaline-Earth Metals on the Structure, Adsorption and Catalytic Behavior of Iron-Based Fischer-Tropsch Synthesis Catalysts](#), *Appl. Catal. A-Gen.*, **464**: 10-19 (2013).
- [28] Yu J., Ge Q., Fang W., Xu H., [Enhanced Performance of Ca-Doped Pt/ \$\gamma\$ -Al₂O₃ Catalyst for Cyclohexane Dehydrogenation](#), *Int. J. Hydrogen Energ.*, **36**(18): 11536-11544 (2011).
- [29] Naseri M., Tahriri Z.F., Taeb A., [The Effect of Ce, Zn and Co on Pt-Based Catalysts in Propane Dehydrogenation](#), *React. Kinet. Mech. Catal.*, **126**(1): 477-495 (2019).
- [30] Tahriri Z.F., Sahebdehfar S., [Effect of Addition of Different Promoters on the Performance of Pt-Sn-K/Al₂O₃ Catalyst in the Propane Dehydrogenation](#), *Iran. J. Chem. Eng.*, **8**(3): 48-54 (2011).
- [31] Lin L.W., Yang W.S.H., Jia J.F., Xu Z.S.H., Zhang T., Fan Y.N., Kou Y., Shen J.Y., [Surface Structure and Reaction Performances of Highly Dispersed and Supported Bimetallic Catalysts](#), *Sci. China Ser. B*, **42**(6): 571-580 (1999).
- [32] Cheng Z.X., Wu Q.L., Li J.L., Zhu Q.M., [Effects of Promoters and Preparation Procedures on Reforming of Methane with Carbon Dioxide Over Ni/Al₂O₃ Catalyst](#), *Catal. Today*, **30**(1-3): 147-155 (1996).

- [33] Horiuchi T., Sakuma K., Fukui T., Kubo Y., Osaki T., Mori T., [Suppression of Carbon Deposition in the CO₂-Reforming of CH₄ by Adding Basic Metal Oxides to a Ni/Al₂O₃ Catalyst](#), *Appl. Catal. A*, **144(1-2)**: 111-120 (1996).
- [34] Sui Z.J., Zhu Y.A., Li P., Zhou X.G., Chen D., [Kinetics of Catalytic Dehydrogenation of Propane over Pt-Based Catalysts](#), *Advances in Chemical Engineering*, **44**: 61-125 (2014).
- [35] Li Q., Sui Z., Zhou X., Chen D., [Kinetics of Propane Dehydrogenation Over Pt-Sn/Al₂O₃ Catalyst](#), *Appl. Catal. A Gen.*, **398(1-2)**: 18-26 (2011).
- [36] Li Q., Sui Z., Zhou X., Zhu Y., Zhou J., Chen D., [Coke Formation on Pt-Sn/Al₂O₃ Catalyst in Propane Dehydrogenation: Coke Characterization and Kinetic Study](#), *Top. Catal.*, **54(13-15)**: 888 (2011).