CHIMIE

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CORRELATION BETWEEN MELTING TEMPERATURES OF ALKALINE EARTH ELEMENTS AND THEIR EFFECT AS PROMOTERS OF Pt-Sn/γ-Al$_2$O$_3$ CATALYST IN PROPANE DEHYDROGENATION REACTION

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Abstract

Pt-Sn/Al$_2$O$_3$ catalyst is well known to have good activity and selectivity for propane dehydrogenation reaction but suffers quick deactivation due to substantial coke formation. In this study effort has been made to improve the characteristics of this catalyst by making tri-metallic catalyst supported on gamma alumina. Pt-Sn-Ca/Al$_2$O$_3$ catalyst was found best among these, especially in yielding improved results in terms of conversion, selectivity, yield and less coke formation. Calcium contents of the catalyst composition were also varied to attain the most suitable amount. Propane conversion, propylene selectivity and yield at optimum operation conditions were: 43.2%, 95.3% and 35.8% respectively at 575 °C. The catalysts were characterized by TEM, XPS, SEM-EDX, H2-TPR, NH3-TPD, CO titration and TGA techniques.

Key words: propane dehydrogenation, Pt-Sn, alkaline earth elements, propylene, coke formation

1. Introduction. Recently propylene demand has increased substantially owing to its vital role in a multitude of chemical applications such as the production of polypropylene, acrylic acid, acrilonitrile, cumene, etc.[1], and hence, necessitates the on purpose propylene production.

At present two catalytic technologies for on purpose production of propylene by catalytic dehydrogenation of propane are used in industry. These technologies use different types of catalysts based on Pt/γ-Al$_2$O$_3$ and on chromium oxide.

It was found that the addition of Sn to Pt/γ-Al$_2$O$_3$ catalyst strongly improves the catalytic activity and selectivity of Pt catalyst and prevents coke formation. The bimetallic Pt-Sn/γ-Al$_2$O$_3$ catalysts have been extensively studied and a number of active and selective catalysts have been developed and patented [2–9]. It is generally agreed that the promoter effect of Sn is a result of combined influence of geometric as well as electronic factors [6, 11, 12]. γ-Al$_2$O$_3$ has been widely used as supporting material for the dehydrogenation catalysts, but its acidity leads to proceeding of hydrocarbons cracking and hence to coke formation.

Efforts are still underway to improve the Pt-Sn/γ-Al$_2$O$_3$ catalyst in order to increase its activity, selectivity and ability easily to be regenerated without appreciable loss of activity [12]. The addition of alkaline earth elements to the catalyst composition change the surface acidity of the catalyst and might be very much beneficial for light paraffins dehydrogenation reaction [13].

In this work, we have studied the influence of the addition of alkaline earth elements (AEE) Mg, Ca, Sr and Ba to Pt-Sn/Al$_2$O$_3$ catalyst on its catalytic and structural properties.

2. Experimental. All studied catalysts were prepared by wet impregnation method in digitally controlled Büchi rotary evaporator Rotavapor (Büchi, Switzerland) equipped with vacuum system. γ-Al$_2$O$_3$ (SAS-200 BASF) with surface area of 185 m^2.g^{-1} and pore volume of 0.47 cm^{3}g^{-1} was used as a catalyst carrier. The flask of Rotavapor was filled up with impregnation water solution containing hydrochloric salts of catalyst components and was heated to 65 °C. The γ-Al$_2$O$_3$ was dried at 120 °C for 3 h and was preheated to 65 °C before it was added to the liquid. The impregnation time was fixed at 4 h. After impregnation, the water was evaporated under vacuum and the solid residue was dried at 120 °C for 2 h. The dried catalytic mass was washed with hot deionized water for removing traces of Cl$^-$ ions. Washed and dried catalyst was then calcined at 600 °C for 6 h. Four catalyst compositions were prepared each containing 1.0 wt % Pt, 1.0 wt. % Sn and 1.0 wt % of the one of AEE (Mg, Ca, Sr, Ba) supported on γ-Al$_2$O$_3$. For comparison a catalyst containing only 1.0 wt % Pt and 1.0 wt. % Sn supported on γ-Al$_2$O$_3$ was prepared.

The synthesized catalysts were tested in PID Micro Activity Test Unit (PID, Spain) in a fixed bed tubular quartz reactor of 9 mm i.d. and 300 mm length. For each run, the reactor was charged with 0.5 g catalyst with particles' size of 0.15–0.25 mm. The catalyst was then in situ reduced with hydrogen flow of 30 cm^3.min^{-1} for 3 h at 575 °C. All catalysts were tested for two-hour reaction time at reaction temperature of 575 °C, Gas Hourly Space Velocity (GHSV) of 3800 h^{-1} and atmospheric pressure. The reaction mixture had a composition of C$_3$H$_8$:H$_2$:N$_2$ = 1:1:5. The used gases C$_3$H$_8$, H$_2$ and N$_2$ were of 99.99% purity.

Y. Alhamed, M. Umar, M. Daous et al.

The parameters characterizing the catalytic activity and selectivity were calculated using the equations (1)–(3) given below.

The conversion of propane X_p was calculated by equation

(1)
$$X_p = (C_f - C_p).100/C_f,$$

where C_f and C_p are the concentration of propane in the feed and in the products respectively.

The propylene selectivity S_p was calculated by equation (2)

(2)
$$S_p = \frac{\text{moles of propylene produced}}{\text{total moles of hydrocarbons at reactor exit}} \cdot 100.$$

The propylene yield Y_p was calculated by

(3)
$$Y_p = X_p.S_p.$$

The amount of carbon deposited on the catalyst during catalytic tests was followed by Thermal Gravimetric Analysis (TGA) and Differential Thermal Gravimetric Analysis (DTA) using TGA/DTA instrument (Netzch, Germany).

H_2-TPR, surface acidity and platinum metal dispersion (determined by carbon monoxide chemisorption) measurements were performed on ChemBet pulsar TPR/TPD, TPO instrument (Quantachrome, USA).

3. Results and discussion. The endothermic propane dehydrogenation (PDH) reaction is equilibrium limited and for attaining high degree of conversion, requires high reaction temperature and low pressure. At these reaction conditions, however, an intensive coke formation on the catalyst surface takes place and fast catalyst deactivation is observed.

Results of activity testing are presented in Fig. 1. Addition of Mg, Ca, Sr and Ba to the catalyst composition has a positive effect on the catalytic properties of Pt-Sn catalysts. The positive effect of the addition of AEE to Pt-Sn catalyst is graded in descending order based on catalyst performance as: Ca > Mg > Sr > Ba. The criterion for this ranking of AEE is a complex taking of the values of X_p, S_p, Y_p and the amount of formed coke into account.

At the beginning of the catalytic test, cracking of propane to methane and ethane took place. This was more prominent in the case of 1.0Pt-1.0Sn/γ-Al$_2$O$_3$ while for Ca and Mg contained catalysts the byproducts were less. As the reaction proceeded, the selectivity was increased and amounts of the byproducts like methane, ethane and ethylene were reduced substantially. After 1 h the steady state is achieved.

From data depicted in Fig. 1, it is clear that the catalytic activity and selectivity of AEE containing of catalysts are higher than those of Pt-Sn/γ-Al$_2$O$_3$ catalysts. Comparing the amount of coke deposited on deactivated Pt-Sn/γ-Al$_2$O$_3$ and catalysts containing AEE shows that presence of AEE and, in particular,
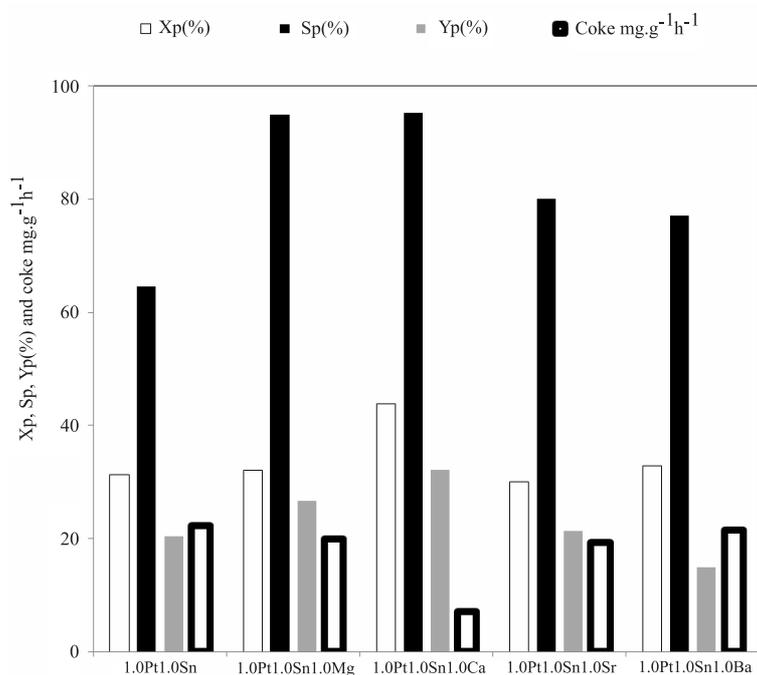
Fig. 1. Effect of alkaline earth metals addition to 1.0Pt-1.0Sn/γ-Al$_2$O$_3$ catalyst on conversion of propane X_p, selectivity to propylene S_p, yield of propylene Y_p and coke formation in mg.gcat^{-1}h^{-1} at 575 °C, GHSV of 3800 h^{-1} and feed ratio of C3H8:H2:N2 = 1.0:1.0:5.0

calcium in the catalyst composition decrease the coke deposition. The effect of AEE presence in the catalyst composition on the coking ability might be due to the facilitated rapid desorption of coke precursors from the metal surface.

The effect of addition of Ca to 1.0Pt-1.0Sn/γ-Al$_2$O$_3$ catalyst was stronger in comparison to the effect of the addition of other AEE, therefore, we have tried to find the optimal Ca content. Figure 2 shows the effect of the amount of calcium addition into the catalyst composition. The influence of the amount of Ca added to the catalyst composition was passing through a maximum of 1.0 wt %, which is equal to the Pt and Sn content. This result indicates that adding calcium in excessive amount probably covers the support surface and may block some of the pores due to the fact that surface coverage and blockage occurs preferentially in smaller pores [14]. The smaller amount of added Ca was not able to modify all acid sites on the alumina surface.

The addition of Ca to the platinum containing catalysts has positive effect on Pt dispersion. It can be seen from the results on Table 1 that calcium containing catalyst had highest Pt dispersion of 52% and smallest Pt particle size of 6.86 Å. The addition of other AEE to the catalyst composition, however, leads to preparation of catalysts with larger particle size than particles in 1.0Pt-1.0Sn/γ-Al$_2$O$_3$.
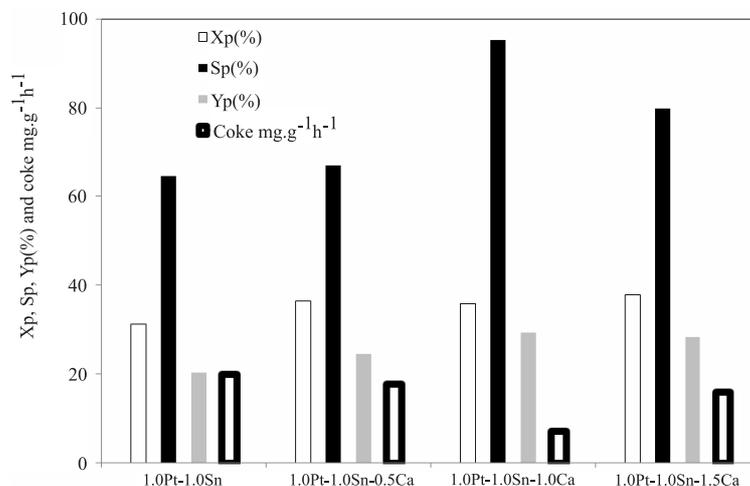
Fig. 2. Effect of the amount of calcium addition to Pt-Sn/γ-Al$_2$O$_3$on propane conversion X_p propylene selectivity S_p, propylene yield Y_p and coke formation in mg.gcat^{-1}h^{-1} at 575 °C, GHSV 3800 h^{-1} and feed ratio of C$_3$H$_8$:H$_2$:N$_2$ = 1:1:5

Nevertheless, the catalysts containing AEE possess improved catalytic activity and selectivity in comparison to Pt-Sn catalyst. Therefore the metal particle size or metal dispersion is not the only decisive parameter which is defining the catalytic properties of Pt containing catalysts.

Another very important factor, which has strong influence on the catalytic activity and selectivity of the metal supported catalysts, is the surface acidity of the used carriers. The addition of AEE to the catalysts' composition resulted in changing the surface acidity of alumina. This is illustrated on Table 1 by presenting the positions of the maxima of the ammonia TPD peaks for alumina, Pt-Sn and Pt-Sn-Ca catalysts. The first two peaks for Pt-Sn-Ca catalysts are shifted to higher temperatures in comparison to the position of those peaks for alumina. However, they appear at lower temperatures than the corresponding peaks for Pt-Sn catalyst. The third high temperature peak for Pt-Sn-Ca catalyst appears again in the temperature zone between those peaks of the other two samples. In this case, however, the lowest temperature was registered for TPD ammonia peak from Pt-Sn sample. These results clearly show that the strength of the surface acid centres has changed due to the presence of Ca thus changing the acidic character of the catalyst. The acidity of γ-Al$_2$O$_3$ is reduced by addition of AEE, which are anchoring on the acid sites of Al^{+3} [15]. It is also reported that pentacoordinated Al^{+3} centres are bonding sites for Pt on γ-Al$_2$O$_3$ because of their strong interaction with atomic platinum or platinum oxide [16,17]. The decrease in acidity contributed to the increased catalyst stability and reduced coke formation and hence led to better performance of 1.0Pt-1.0Sn-1.0Ca/γ-Al$_2$O$_3$ catalyst.

Pt dispersion results from CO chemisorption for various catalysts and positions of maxima
of NH$_3$ desorption peaks

Catalyst	Pt dispersion %	Pt average crystallites size Å	Pr surface area m^2/g	Temperatures of NH$_3$ desorption peaks maxima °C		
				1st peak	2nd peak	3rd peak
γ-Al$_2$O$_3$	–	–	–	166.0	303.0	503
1.0Pt-1.0Sn/γ-Al$_2$O$_3$	44.20	8.18	1.10	208.0	313.0	488.0
1.0Pt-1.0Sn-1.0Mg/γ-Al$_2$O$_3$	33.07	11.42	0.82	–	–	–
1.0Pt-1.0Sn-1.0Ca/γ-Al$_2$O$_3$	52.05	6.86	1.36	178.0	307.0	498.0
1.0Pt-1.0Sn-1.0Sr/γ-Al$_2$O$_3$	16.36	23.08	0.40	–	–	–
1.0Pt-1.0Sn-1.0Ba/γ-Al$_2$O$_3$	18.87	20.01	0.47	–	–	–

In attempt to find explanation for the observed influence of AEE on the catalyst properties, we have found that a correlation exists between the melting points of AEE arranged according to their increased atomic number and the effect of addition of AEE on the catalytic properties of Pt-Sn catalysts in reaction of propane dehydrogenation.

In Figure 3 we have plotted on different curves of AEE melting points, parameters characterizing catalytic performance of catalysts containing different AEE (x_p, S_p, Y_p amount of coke formed and propylene yield for long run tests Y_{pstab}) and Pt dispersion. The curve of the melting points as well as all other
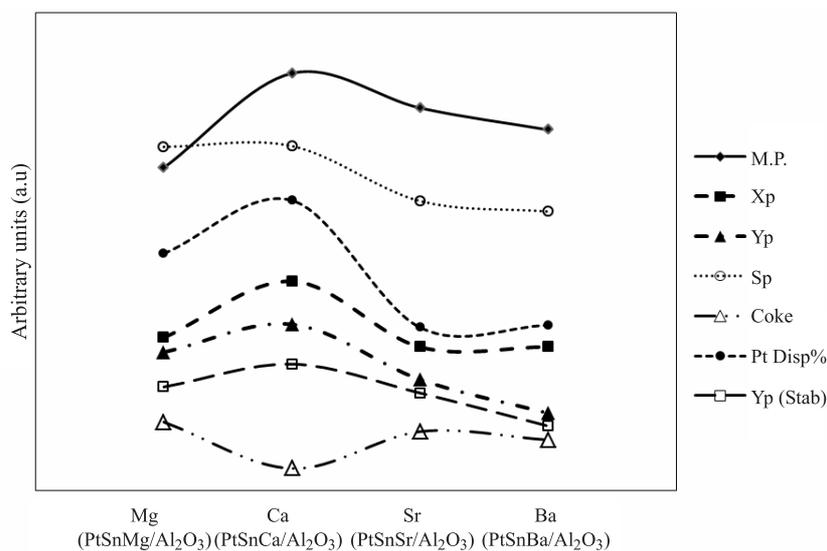

Fig. 3. Correlation of the melting points of AEE with catalytic properties of
catalysts promoted by AEE

Y. Alhamed, M. Umar, M. Daous et al.

curves pass through the maxima located at calcium. The exception of this rule is the curve for the formed coke amount, which has a minimum for Ca containing catalysts.

AEE have very close chemical properties, therefore the reasons for the differences of the effects of AEE addition on catalytic properties of Pt-Sn catalysts should have a complex character including chemical as well as other factors. One of the possible explanations of the observed correlation can be described as follows.

In order to stabilize Pt nanoparticles on the carrier surface in Pt/γ-Al_2O_3 catalyst, it is necessary to add to the catalyst composition a metal with low melting point [18]. The positive effect of adding Sn with melting point of $232\,°C$ and Pb with melting point $328\,°C$ to Pt catalyst is well established. The Pt-Sn$/\gamma$-Al_2O_3 catalysts were successfully used for many years in the process of gasoline reforming. This process is carried in the temperature interval 490–$530\,°C$. The addition of the low melting point element Sn to the catalyst composition was to prevent the highly dispersed Pt particles from aggregation and easily form with Pt compounds like Pt_3Sn, which is regarded by many authors also active in the gasoline reforming process.

The process of propane dehydrogenation over Pt-Sn catalyst is carried out at temperature interval of 600–$650\,°C$. These temperatures are much higher than the temperature at which Pt-Sn catalyst is used in the hydrocarbon reforming process. Therefore in order to preserve the high catalytic properties of the Pt-Sn system, it is necessary to stabilize it by adding a new component with appropriate melting temperature. The melting temperatures of Mg, Ca, Sr and Ba are 650, 842, 777 and $727\,°C$ respectively. Calcium, which has the highest melting temperature between all AEE is an optimal choice for the stabilizing Pt-Sn system between all AEE.

Positive effects of Ca addition to Pt-Sn$/\gamma$-Al_2O_3 composition on the catalyst properties propane dehydrogenation reaction can be attributed to:

- Increasing of the thermal stability of the catalyst that arises from the formation of a protective layer between the support and active metal, which also inhibits the formation of inactive phases [19];
- Interaction of Ca with Pt forming $CaPt_2$ and with γ-Al_2O_3 support. The result is the reduction of the metal-support interaction and better performance of the catalyst;
- Addition of Ca to Pt-Sn catalyst leads to the formation of Pt particles with highest dispersion. Ca containing Pt-Sn catalysts have shown the best catalytic properties between all promoted by AEE catalysts;
- Depression of the process of coking. Ca is easily dispersed on the catalyst surface leading to uniform distribution due to surface diffusion. At the same time calcium, because of its mild basic character and low density is adsorbed on acid centres of γ-Al_2O_3 thus depressing the coke formation.

The obtained correlation can be used as a qualitative criteria for selection of the most suitable Pt catalysts in the hydrogenation-dehydrogenation catalytic processes.

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