Highly Active and Selective $PtSnM_1/\gamma\text{-}Al_2O_3$ Catalyst for Direct Propane Dehydrogenation

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Summary: This study is aimed to understand the role of alkaline earth elements (AEE) to the catalytic performance of $PtSnM_1/\gamma\text{-}Al_2O_3$catalystfor the direct propane dehydrogenation (where M_1 = Mg, Ca, Sr, Ba). All the catalysts were prepared by using wet impregnation.The overall catalytic performance of all the catalysts was studied at different reaction temperatures, feed composition ratios and GHSV. The best operating reaction conditions were575°C, feed composition ratio of $C_3H_8:H_2:N_2$ = 1.0:0.5:5.5 and GHSV of $3800h^{-1}$. An optimal addition of "Ca" to $PtSn//\gamma\text{-}Al_2O_3$ catalyst, enhanced the catalytic activity of $PtSnM1/\gamma\text{-}Al_2O_3$ catalyst in comparison to other studied AEE. This catalyst had shown the highest propane conversion (~ 55.8 %) with 95.7 % propylene selectivity and least coke formation (7.11 $mg.g^{-1}h^{-1}$). In general, the increased catalytic activity of $PtSnM_1/\gamma\text{-}Al_2O_3$ is attributed to the reduced coking extent during the reaction. In addition, the enhanced thermal stability of the $PtSnCa/\gamma\text{-}Al_2O_3$catalystis because of the protective layer between$\gamma\text{-}Al_2O_3$ and active metal, which allows the formation of active species such as PtSn, $PtCa_2$ and Pt_2Al phases?

Keywords:$PtSnM_1/\gamma\text{-}Al_2O_3$,Propane dehydrogenation, Alkaline earth elements, Promoters.

Introduction

Propane dehydrogenation is an endothermic process. To achieve an acceptable high level of propylene yield, it requires high reaction temperatures and low propane partial pressure. Usually, at such high temperatures, formed coke due to thermal and catalytic cracking of hydrocarbons lead to decreased olefin yield and enhanced catalyst deactivation.

A wide range of elements were tested as active components of supported metal catalysts for propane dehydrogenation such as noble (Pt, Pd, Ru, Rh, Au, etc.) or transition (Ni, Fe, Co, Cu etc.) metals. In some cases, oxide systems were also used. Different supports such as oxides, spinel [1-3], aluminates [4], MgO [5], silica [6], titania and zirconia [7] had been investigated as potential support of the catalyst.

Based on available literature, oxides of iron, chromium and platinum supported on $\gamma\text{-}Al_2O_3$ were widely used [8-12]. However, the quality of the used catalysts still needs substantial improvements.

One of the most effective ways to achieve this aim is the promotion of $Pt/\gamma\text{-}Al_2O_3$ system by different promoters like elements with low melting temperature (such as Sn, Pb, In, Ga, Ge), transition elements, alkaline and alkaline-earth elements. In general, Sn is known as best promoter to $Pt/\gamma\text{-}Al_2O_3$ catalyst. Therefore, the $Pt\text{-}Sn/\gamma\text{-}Al_2O_3$ becomes logically a favourable catalyst for future attempt to prepare improved catalyst for propane dehydrogenation.

Depending upon the composition of the catalysts and reaction conditions, different reaction mechanisms for propane dehydrogenation reaction on Pt containing catalysts were proposed. For example, in the case of dehydrogenation on very diluted Pt-Au alloys catalyst[13] the mechanism envisagethe dissociative chemisorption of propane on a single platinum atom, to which two others adsorption sites are associated. The one of them adsorbs a hydrogen atom. Later, subsequent conversion of the propyl radical into π-bonded propene via β-hydrogen elimination takes place. In addition, Kondarides *et al.,* [5] suggested that above 400 ºC, bonds formation between precious metal and each component of the support (such as Pt-O, Pt-Mg bonds in Pt/MgO catalyst and Mo-O and Mo-Mg for Mo/MgO catalyst) were responsible for the enhanced catalytic activity.

The addition of alkali metals to the $Pt/\gamma\text{-}Al_2O_3$ catalysts significantly affects the catalytic properties of the catalysts. Padro *et al*[14] concluded that addition of K to Pt/Al_2O_3 and $PtSn/Al_2O_3$ can significantly decrease the catalyst deactivation and

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enhanced catalytic activity due to presence of Sn. Bocanegra *et al*[15] suggested that the stability of such catalyst could be attributed to the potential changes in the surface acidity because of the modification of surface of the used carrier.

Fewer studies [12, 16-19] reported data on the impact of the presence of transition metals (such as Zn, Cr and Ce) in the catalyst composition to the catalytic properties of either Pt/γ-Al_2O_3 or PtSn/γ-Al_2O_3catalyst. The presence of Cr [16]in the form of Cr^{+3}, significantly improved the synergistic effect between PtSn during the catalytic propane dehydrogenation. Whereas, presence of Ce [17] improves the overall catalytic performance of PtSn/γ-Al_2O_3catalyst and its stability. In general, the addition of selected transition metals significantly improves the overall catalytic performance for propane dehydrogenation[16].

Because of high reaction temperature, the catalyst life is hampered due to the formation of coke. It was established that three types of coke are formed[2, 20-33]: (i) coke on and/or in the vicinity of the metal surface; (ii) coke on the catalyst carrier; and (iii) graphitic coke formed on the Pt or on the catalyst carrier. Both Sn and alkali metals (Li, Na and K) may reduce the formation of coke on the catalyst active sites. In general, combination of alkali and alkaline earth metal [34] to the support during the catalyst preparation, decreases the support acidity which ultimately reduces the chances of coke formation.

Based on the available literature, as per author's knowledge, none of the systematic studies has been reported on the presence of individual alkaline earth element impact and identification of best alkaline earth element to the: (i) catalytic activity for direct propane dehydrogenation and (ii) on the stability of PtSn/ γ-Al_2O_3 catalysts at temperature of 575 ºC. Therefore, this study is aimed to investigate the aspects associated with the promotion of PtSn/γ-Al_2O_3 catalysts by alkali earth elements such as Ca, Mg, Sr and Ba on the enhancement of propylene yield, catalyst selectivity and prevention of the quick deactivation by coke formation.

Experimental

Materials

The following chemicals were used:γ-aluminum oxide SS-200 (BASF Chemicals), Platinum Chloride (ACROS Organics), Stannous Chloride ($SnCl_2.2H_2O$; BDH) Magnesium Chloride ($MgCl_2$; Hopkin & Williams), Calcium Chloride ($CaCl_2$; MERCK), Strontium Chloride ($SrCl_2.6H_2O$;Merck) Barium Chloride ($BaCl_2.2H_2O$; Hopkin & Williams) and Deionized water (DIW).

Catalyst Preparation

Wet impregnation method is used to prepare all the catalyst samples. For this, digitally controlled Buchi rotary evaporator, equipped with reflux and vacuum system was used. The γ-Al_2O_3grains were crushed in a ball mill and powder fraction composed of0.125 to 0.25 mm grain size was selected and dried for 3 hours at 120 ºC. The required amount of the γ-$Al_2O_3$was preliminary heated to 65°C and then transferred in the rotavapor flask. The precise amounts of each active metal chloride salts were used. The chlorides solutions were mixed and added simultaneously in the rotavapor flask containing the catalyst support.

The impregnation was conducted at 65 °C for 4 hours followed by vacuum drying until semi dry sludge was obtained. After filtration, the sludge was rinsed many times with DIW until the Cl^- ions were washed. The removal of chloride anions was assured by using test with $AgNO_3$solution. The washed sludge was then dried at 120 °C for 3 hours followed by calcination at 650°C for 6 hours in digitally controlled furnace. The calcined material was crushed and then tableted. Tablets were crushed and fraction of required particle size 125-250 µm was selected. The list of prepared catalysts was summarized in Table-1.

Table 1: List of prepared catalysts.
Enrollment in local colleges, 2005

College	New students	Graduating students	Change
	Undergraduate		
Cedar University	110	103	+7
Elm College	223	214	+9
Maple Academy	197	120	+77
Pine College	134	121	+13
Oak Institute	202	210	-8
	Graduate		
Cedar University	24	20	+4
Elm College	43	53	-10
Maple Academy	3	11	-8
Pine College	9	4	+5
Oak Institute	53	52	+1
Total	**998**	**908**	**90**

Source: Fictitious data, for illustration purposes only

Catalyst carrier's characterization

BET surface area measurements

Pore volume and surface area of used γ-Al_2O_3support and of the prepared catalysts were measured by BET method using Quantachrome Nova

2000 instrument, USA. Before each measurement, the samples were heated at300ºCin vacuum for 5 h.

Temperature Programmed Reduction by H_2 (TPR - H_2)

TPR - H_2 was performed on QuantachromeChemBet Pulsar. The sample (0.2 g) was charged into the instrument cell. At first it was dried at 150 ºC for one hour and then cooled to 40 ºC under N_2 flow. Later on, TPR- H_2 was studied with a flow of mixture (10% H_2: 90% N_2) and under temperature ramping of 10 ºC min^{-1} up to final temperature 650 ºC.

Temperature Programmed Desorption of ammonia (TPD- NH_3)

Acidic character of prepared samples was elucidated using NH_3TPD. Before the measurements, the samples (0.2 g) were first dried at 150 ºC for one hour under N_2 flow and then reduced with pure hydrogen (60 cm^3 min^{-1}) for 3 hours. Then the sample was flushed with He. The sample was then saturated by pure NH_3 for half an hour. Desorption was performed using a He flow of 80 $cm^3 min^{-1}$ and temperature ramping of 10 ºC min^{-1} up to final temperature 600 ºC.

Metal dispersion measurement by CO-pulse titration

Platinum metal dispersion and its crystallite size were determined by CO-pulse titration using ChemBet Pulsar instrument. A. 0.2 g sample was charged into the sample cell and at first was reduced in situ with hydrogen at flow of 60 $cm^3 min^{-1}$and then cooled to 40 °C. Pulses of CO with fixed volume were programmed to be injected after specified intervals into cell containing the reduced catalyst until the saturation achieved. Exit gases from the sample cell were analyzed by a TCD of the instrument. It was accepted that the CO adsorption Pt is one molecule CO adsorbs on one surface Pt atom.

XPS Studies

Surface concentration of the elements in the catalysts was determined by XPS technique. Small quantity of sample was mounted on sample holder with double sided non-conducting carbon tape. The samples were excited by a non-monochromatic X-Ray source (MgKα-300W) using SPECS Phoibos 150 MCD-9 analyzer (Germany) equipped with Auger electron microscope. For actual measurement, the analyzer was set to medium magnification lens mode with a round entrance slit of 7 mm diameter and the IRIS aperture was closed to 30 mm. The acceptance angle of the analyzer was about ± 6º.

Catalyst activity testing

The synthesized catalysts were tested in PID Micro Activity Test Unit (Spain) by using fixed bed flow tubular quartz reactor (10 mm inside diameter, 300 mm length, charged with 0.5 g catalyst having particle size between 0.125 and 0.25 mm) at atmospheric pressure. Catalyst was placed at the center of the reactor and the space above and below the catalyst was filled with grounded α-alumina to prevent the coke formation from free radicals formed from hydrocarbons due to thermal cracking in the empty reactor volume at high reaction temperatures. Reaction temperature was monitored by thermo couple located into the catalyst bed.The temperature was controlled within ± 1 °C. The gas flows were controlled by Bronkhorst Mass Flow Controllers within ± 1% error.

Catalyst reduction

After loading the catalyst sample in the reactor, it was flushed with nitrogen (flow rate of 50 $cm^3 min^{-1}$at temperature of120 °C) and was kept at that temperature for 2 hours. Later, the nitrogen flow was replaced by mixture of 5 % hydrogen and 95.0 % nitrogen. Then temperature was increased to 200 °C and was kept constant for 1 hour. Then the temperature was increased again at ramping rate of 3 ºC min^{-1}. After every 50 °C temperature rise, the hydrogen content in the gas flow was increased by 5 %. Finally, at 600 °C, the catalyst was reduced for 3 hours in the presence of H_2.

Catalytic Reaction Conditions

Most of the catalytic tests were performed at Gas Hourly Space Velocity (GHSV) 3800 h^{-1}; reaction temperature in therange of 540 - 600 °Candthe reaction mixture composition at the reactor inletwas C_3H_8:H_2:N_2 = 1:1:5. Overall, propane conversion (X_p), selectivity (S_p), propylene yield (Y_p) was calculated. The amount of deposited cokeon the used catalyst was measured by coke burning in TGA instrument.

Reaction Product Analysis

A gas chromatograph (SRI 8610C, USA) equipped with both FID and TCD detectors was employed to analyze the reaction products such as C_3H_8, C_3H_6, C_2H_6, C_2H_4, $CH_4$by using alumina column (I.D:3.175 mm; Length: 1.7 m; treated with 5% KCl) under highly pure N_2 flow.

Results and Discussion

Catalytic Activity

Alumina's acidic nature was well known and presence of acidic sites, in general, promotes the coke formation at the surface of the catalysts. To reduce coke formation, we have modified the Pt-Sn/γ-Al_2O_3 by adding a series of Alkaline Earth Elements (AEE) such as Mg, Ca, Sr and Ba. Several parameters such as catalytic activity, selectivity for propylene, yield of propylene, coke formation, and stability were studied and results are summarized in Fig1 and Table 2.

Table-2: Effect of AEE addition to PtSnCa/γ-Al_2O_3catalyst at feed ratio of C_3H_8:H_2:N_2=1:1:5 , GHSV = 3800 h $^{-1}$ reaction temperature = 575°C after two hours of time on stream

College	New students	Graduating students	Change
	Undergraduate		
Cedar University	**110**	**103**	**+7**
Elm College	**223**	**214**	**+9**
Maple Academy	**197**	**120**	**+77**
Pine College	**134**	**121**	**+13**
Oak Institute	**202**	**210**	**-8**
	Graduate		
Cedar University	**24**	**20**	**+4**
Elm College	**43**	**53**	**-10**
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Pine College	**9**	**4**	**+5**
Oak Institute	**53**	**52**	**+1**
Total	**998**	**908**	**90**

Enrollment in local colleges, 2005

Source: Fictitious data, for illustration purposes only

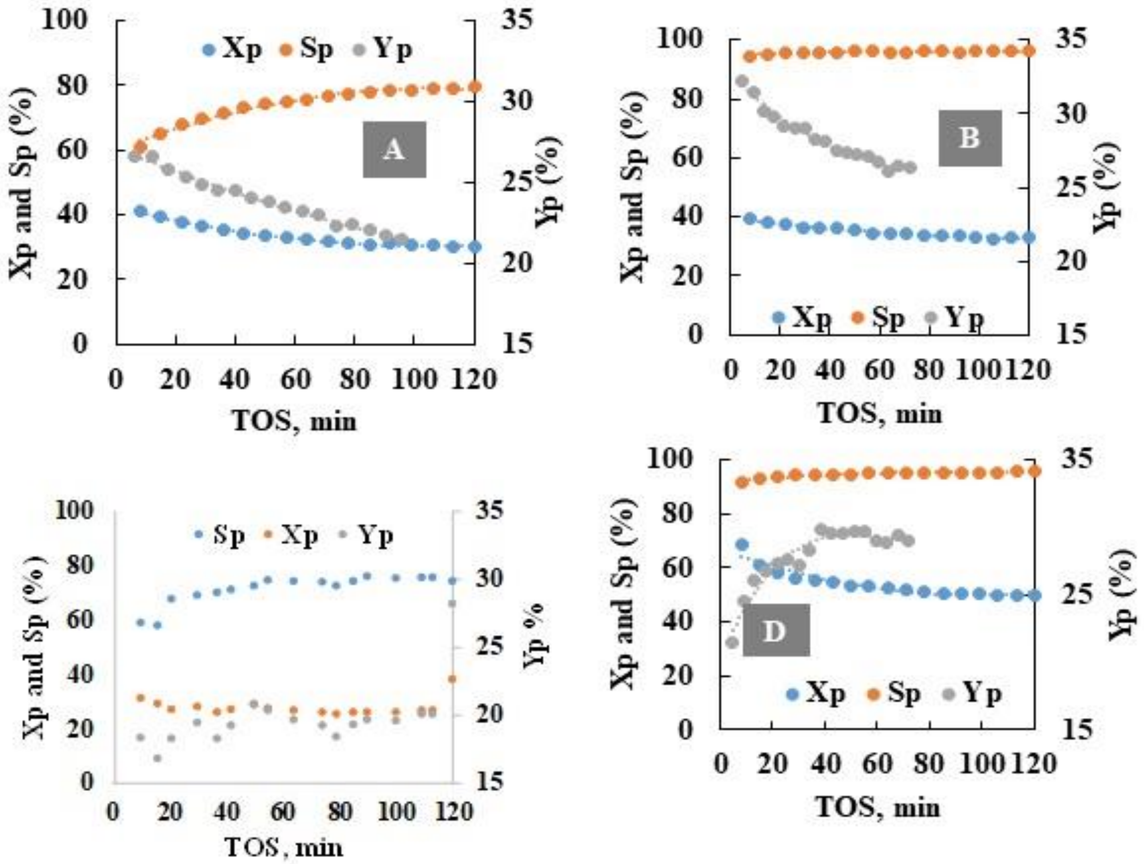

Fig1: Effect of AEE addition to PtSn/γ-Al_2O_3on propane conversion (Xp), propylene selectivity (Sp) and propylene yield (Yp)at 575 °C, GHSV 3800 h $^{-1}$ and feed ratio of C_3H_8:H_2:N_2=1:1:5. A: Effect of Sr; B: Effect of Mg; C: Effect of Ba and D: Effect of Ca.

Fig.1 shows a detailed comparison of the catalytic activity of PtSnMg/γ-Al_2O_3, PtSnCa/γ-Al_2O_3, PtSnSr/γ-Al_2O_3 and PtSnBa/γ-Al_2O_3catalysts in terms of overall propane conversion (X_p), propylene selectivity (S_p) and propylene yield (Y_p). Results showed that presence of AEE had a remarkable impact on the afore-mentioned parameters of catalysts performance. Among all tested samples, the PtSnCa/γ-Al_2O_3catalyst had shown the highest propane conversion of 55.8% and95.2 % propene selectivity within obtained hydrocarbons. In addition, it demonstrated least coke formation of 7.11 mg^1 $g^{-1}h^{-1}$, which was 64% less than the coke formed during the use of PtSn/γ-Al_2O_3catalyst under similar reaction conditions.

In comparison, the presence of Ba had the strongest negative effect on the catalyst performance. Whereas, the presence of both Mg and Sr in PtSn/γ-Al_2O_3 had almost shown similar percentage of propane conversion and coke formation as to that of PtSn/γ-Al_2O_3 alone. However, the catalyst containing “Mg” exhibited higher propene selectivity as to the catalyst containing “Sr”. In comparison, the addition of “Ca” to PtSn/γ-Al_2O_3 enhanced both % conversion as well as propene selectivity with least coke formation. Even after two-hour reaction time, there was no appreciable decrease in total degree of conversion in addition to consistent % yield. In general, the overall catalytic performance during propane dehydrogenation reaction was enhanced by the addition of AEE in catalyst composition the order of Ca>Mg>Sr>Ba.

Impact of PtSnCa/γ-Al_2O_3composition on overall catalytic performance

To investigate the impact of the amounts of each component of the best catalyst, different amount of “Ca” was added to two reference catalysts 0.5Pt0.5Sn/γ-Al_2O_3 (named as reference catalyst A) and PtSn/γ-Al_2O_3 (named as reference catalyst B). Two different amounts 0.5 % wt Ca and 1.5% wt Ca were added to reference catalyst sample A and three different amounts0.5%wt Ca, 1.0%wt Ca and 1.5%wt Ca were added to reference catalyst sample B.

Under similar reaction conditions (575 ˚C, GHSV 3800 h^{-1} and feed ratio of $C_3H_8:H_2:N_2 = 1:1:5$), all the seven catalysts A, 0.5%Ca/A , 1.5%Ca/A, B, 0.5%Ca/B, 1%Ca/B and 1.5% Ca/B were tested and obtained product stream composition results are summarized in Table-3.

Table-3: Composition of all reaction products for various catalysts at 575 °C, GHSV 3800 h^{-1} and feed ratio of $C_3H_8:H_2:N_2=1:1:5$

Enrollment in local colleges, 2005

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Total	**998**	**908**	**90**

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The 0.5%Ca/A has shown higher propane conversion (38.3%) as to that of 1.0%Ca/B (35.8%). However, 1% Ca/B produces highest yield of propylene (29.8%) with least coke formation in comparison to 0.5% Ca/A. In addition, the propylene selectivity (Sp) was slightly lesser as to that of0.5% Ca/A(95.2 % compared to 97.6 %), that could be attributed to higher cracking extent (see the product distribution mentioned in Table-3). Nonetheless, on catalyst 0.5% Ca/A, the rate of coke formation was almost twice as much as that obtained with catalyst 1% Ca/B.

In general, the catalysts 1%Ca/B was found to be the best among other studied catalysts (A, 0.5% Ca/A, 1.5% Ca/A, B, 0.5% Ca/B, and 1.5% Ca/B). A clear indication that an optimum amount Ca had played a key role in the overall propane dehydrogenation catalytic activity of PtSnCa/γ-Al_2O_3 catalyst.

Effect of reaction temperature

To find an optimal reaction temperature condition, for obtaining the highest propylene yield and selectivity, the catalytic dehydrogenation of propane, experiments were performed at three different temperatures of 550 ˚C, 575˚C and 600 ˚C[Fig. 2].

At 550 °C, both conversion as well as yield was much lowers as to those obtained at 575 °C and 600 ˚C. Whereas, at 600 ˚C, although the conversion was high at the onset of the reaction, but it underwent a sharp decline that could be attributed to the fast deactivation due to coke deposition. However, this phenomenon was not observed at 550˚C and 575˚C. A clear indication of both cracking reactions and reactions leading to coke deposition were more prominent at high temperatures.

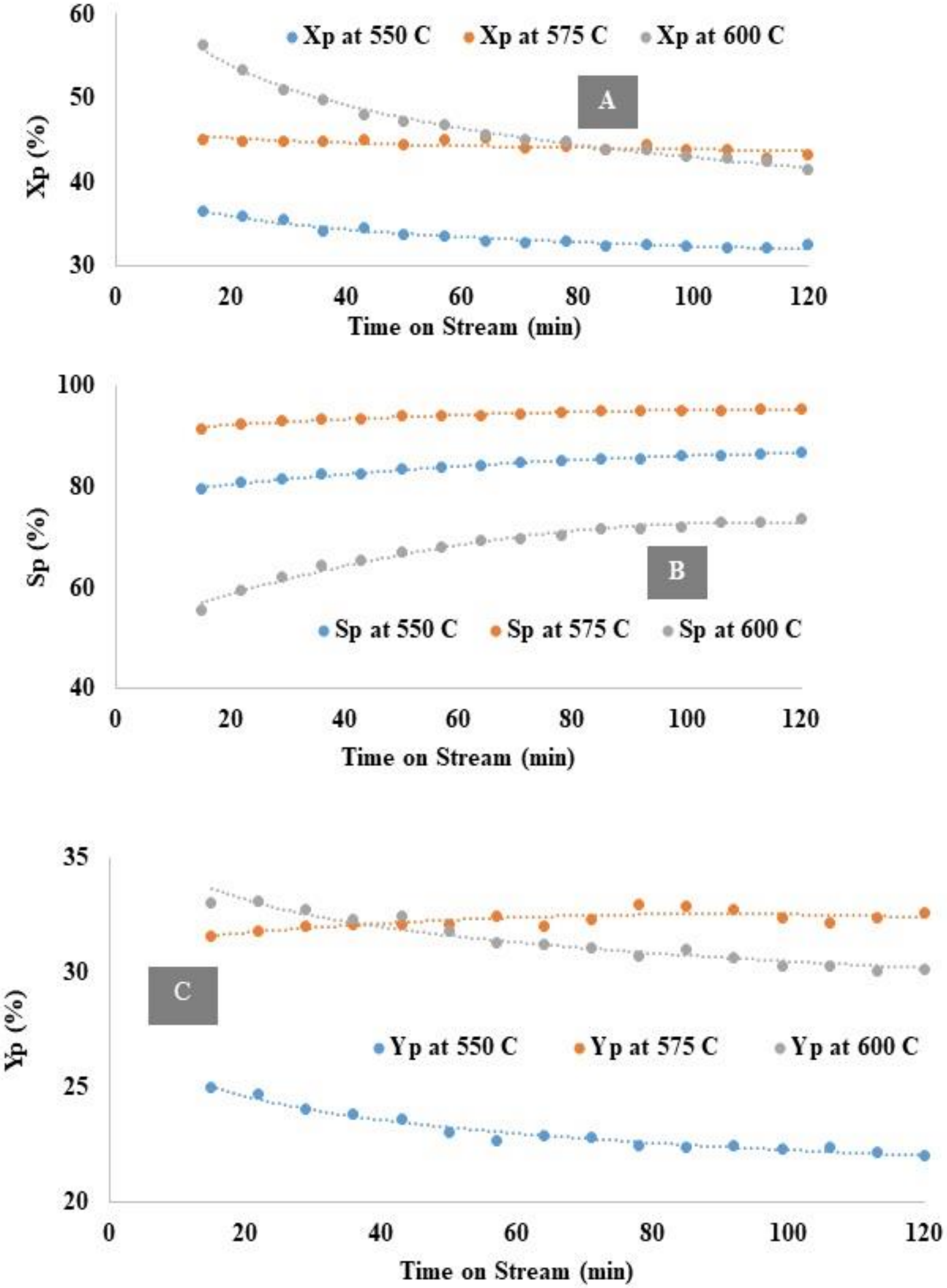

Fig. 2: Effect of temperature on A: propane conversion (Xp); B: propylene selectivity (Sp) and C: propylene yield (Yp) for catalyst PtSnCa/γ-Al_2O_3at 550, 575 and 600 °C, feed ratio of C_3H_8:H_2:N_2=1:1:5 and GHSV of 3800 h^{-1}

At 575°C, conversion was constant even after 2 hours of reaction time- an indication of good catalysts stability. It was also clear (see Fig. 2B) that propylene selectivity was maximal at temperature 575 °C (~95%) and much better than other studied temperatures. The propylene yield exhibited the similar pattern, and temperature of 575 °C provided the maximum yield of about 32.5% initially and was relatively consistent throughout the reaction for 2 hours. Hence, temperature of 575 °C was found to be optimal for this catalyst and all the subsequent experimentation for finding the other optimal operating conditions were conducted at this temperature.

Effect of Hydrogen concentration intheinitial reaction mixture

The effect of hydrogen concentration in the initial reaction mixture on propane conversion (X_p), propylene selectivity (S_p) and its yield (Y_p) were studied at three different initial reaction mixtures with different volume ratios;C_3H_8:H_2:N_2 = 1.0:0.25:5.75; 1.0:0.5:5.5 and 1.0:1.0:5.0. For this study, both the reaction temperature and GHSV were 575 °C and 3800 h^{-1}respectively.

The obtained results are shown in Fig. 3. Both the lower and higher hydrogen to propylene ratio were not favorable for better propylene yield. Both, the conversion and yield followed almost the same trend for each ratio, but the selectivity was much lower in the ratio 1:0.25:5.75.

Selectivity for initial reaction composition of 1:0.5:5.5 and 1.0:1.0:5.0 were comparable but the yield was far better for 1:0.5:5.5 composition and remain almost constant during reaction time, while for other molar feed ratios it gradually decreased with time.

According to thermodynamics, the addition of hydrogen to the reaction mixture will depress the propane dehydrogenation reaction. On the other hand, hydrogen addition to the reaction mixture reduces the coke formation and therefore reduces the catalyst deactivation. Obviously, the ratio of H_2/C_3H_8 was very vital. High ratio reduces the rate of deactivation but gives moderate conversion while lower ratio accelerates the deactivation of catalyst thereby decreasing the yield. Therefore, an intermediate ratio of hydrogen to propane should be more favorable to improve the catalyst performance. Mostly researchers such as Bai *et al.*[35] had used H_2:C_3H_8 ratio 0.25but our finding indicates that H_2:C_3H_8 ratio of 0.5 was most promising for propane dehydrogenation reaction on PtSnCa/γ-Al_2O_3catalyst.

Effect of Gas Hourly Space Velocity (GHSV)

To investigate the GHSV effect , catalytic propane dehydrogenation was carried at three different GHSV: 1900 h^{-1}, 3800 h^{-1}, and 5700 h^{-1} under best reaction conditions (575 °C and molar feed ration C_3H_8:H_2:N_2 = 1.0:0.5:5.5).

For total GHSV of (1900 h^{-1}), the overall propylene selectivity was poor, and it was increased gradually to 60% after 2 hours reaction time. However, the corresponding propane conversion exhibited a very fast decline with time that might be because of rapid deactivation due to coke deposition on the catalyst. An indication longer contact time between the catalyst and reactants (low GHSV) has adverse effect on the selectivity. Most probable, it was due to the unwanted reactions such as hydrocarbon hydrogenolysis and cracking. Though, under this GHSV, the initial propane conversion was reasonably high, but the existences of other light hydrocarbons such as CH_4, C_2H_6 and C_2H_4, (20.2%, 8.1% and 1.3% respectively; Fig. 5) produced though hydrogenolysis and cracking was responsible for the reduced selectivity to propylene.

For a higher GHSV (5700 h^{-1}), the overall propylene selectivity was higher as to that of GHSV 1900 h^{-1}. Initially it increased with reaction time and attains a maximum selectivity of 86%. However, at this GHSV, an adverse effect was noted on the overall propane conversion which was far lower than obtained under GHSV of 1900 h^{-1}. In comparison to GHSV of 1900 and 5700 h^{-1}, the GHSV of 3800 h^{1} had shown an overall increased propylene selectivity and yield of 95.7% and 35.8 % respectively; see Fig.4)with slightly lower conversion (44.3%) as to that of attained under GHSV 1900 h^{-1}. Thus, an intermediate GHSV of 3800 h^{-1} was favorable for better catalyst performance. Therefore, for the PtSnCa/γ-Al_2O_3 catalyst, the optimum reaction conditions are 575 °C with molar feed ratio of C_3H_8:H_2:N_2 = 1.0:0.5:5.0under GHSV of 3800 h^{-1}.

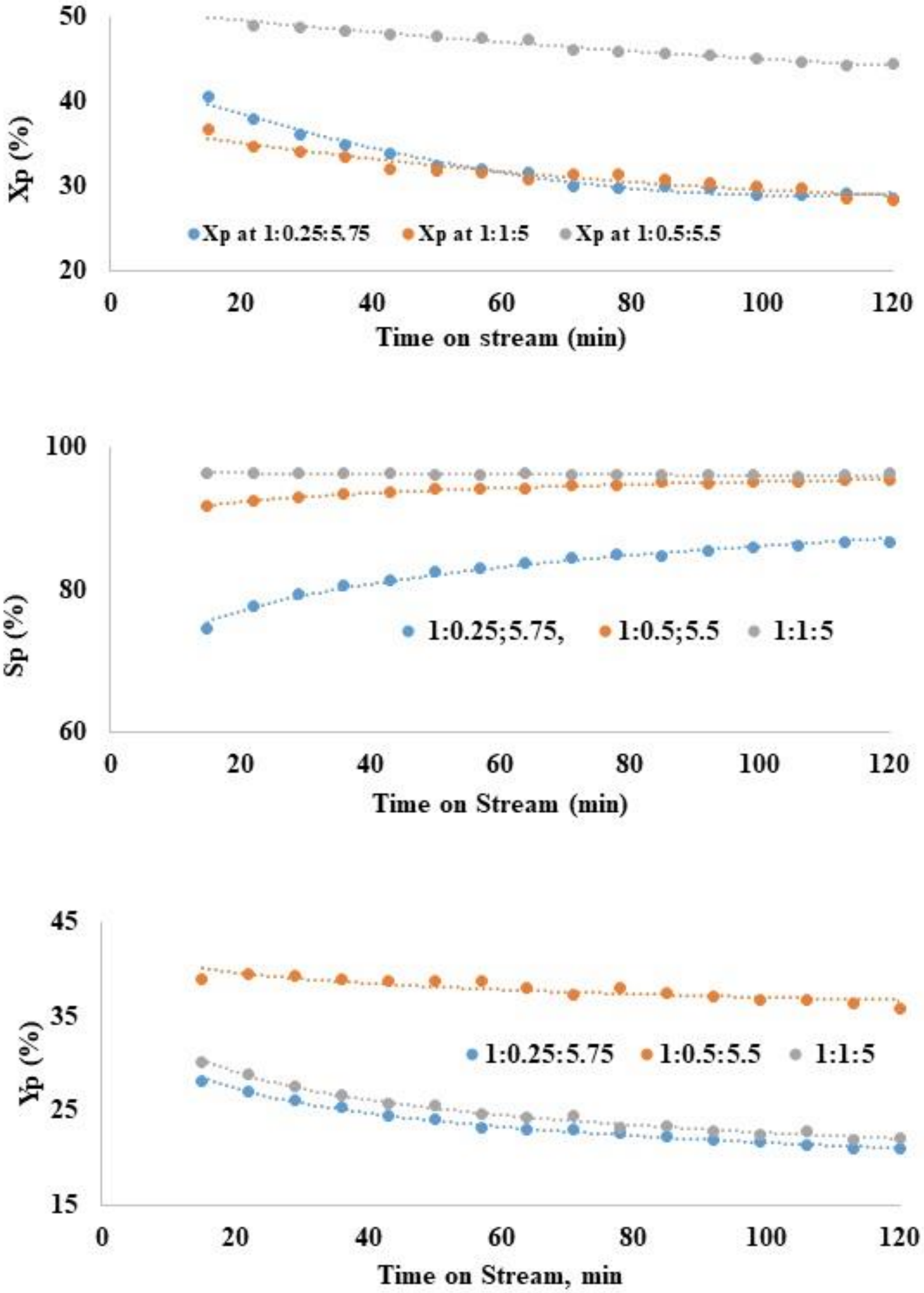

Fig. 3: Effect of molar feed ratio of reactants on propane conversion Xp, propylene selectivity Sp and propylene yield Yp for PtSnCa/γ-Al_2O_3at 575 ºC at threedifferent feed ratios and GHSV of 3800 h^{-1}

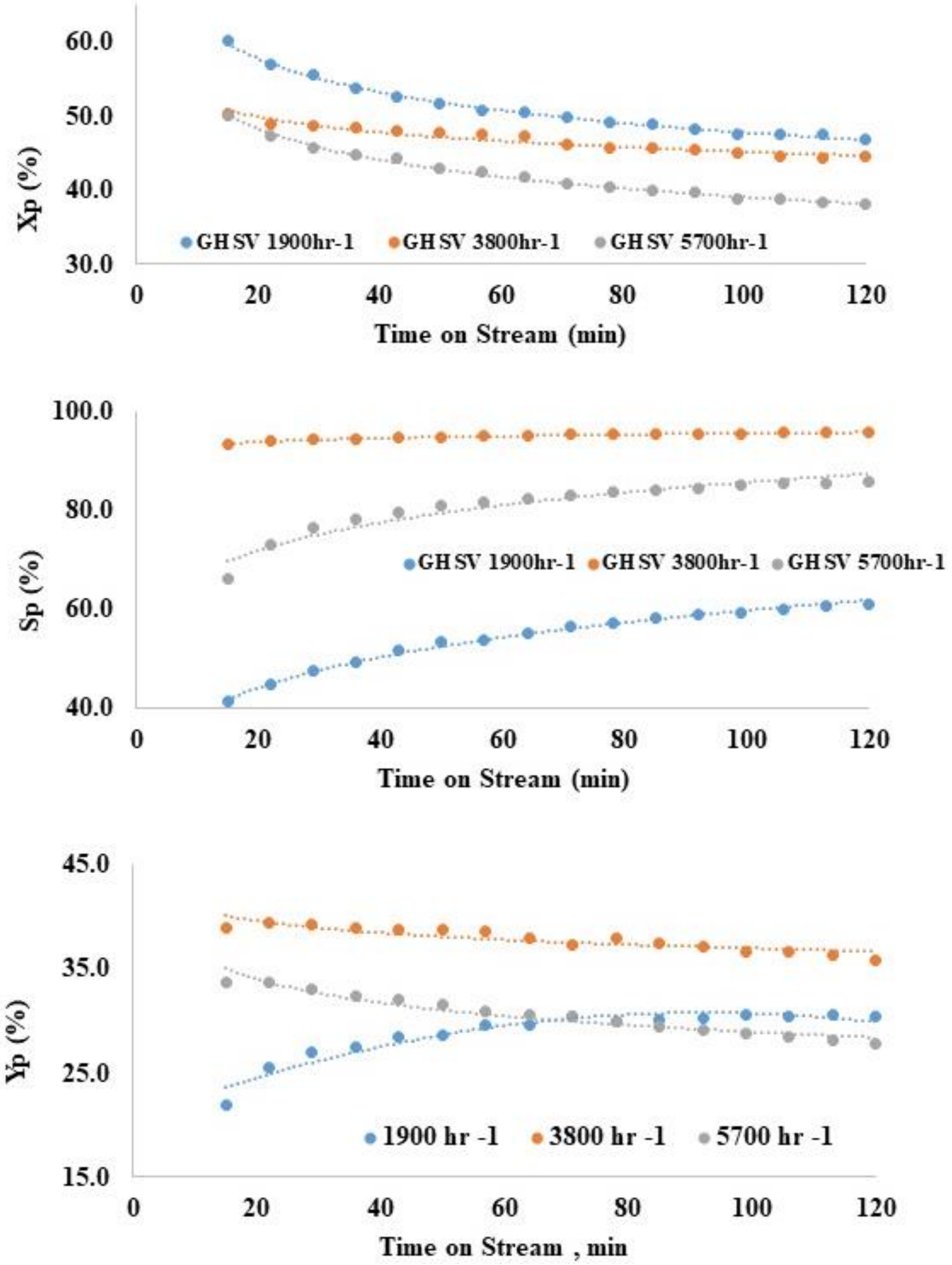

Fig. 4: Effect of GHSV on propane conversion (Xp), propylene selectivity (Sp) and propylene yield (Yp) for PtSnCa/γ-Al_2O_3at 575 ºC and feed ratio of C_3H_8:H_2:N_2=1:1:5.

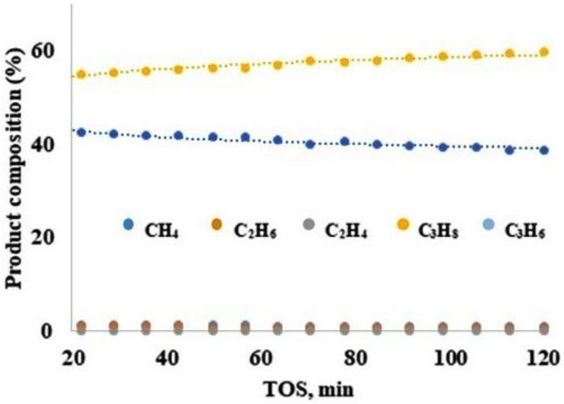

Fig. 5: Product compositions for propane dehydrogenation at 575 °C, molar feed ratio C_3H_8:H_2:N_2=1:0.5:5.5 and GHSV 3800h^{-1} for PtSnCa/γ-Al_2O_3 catalyst.

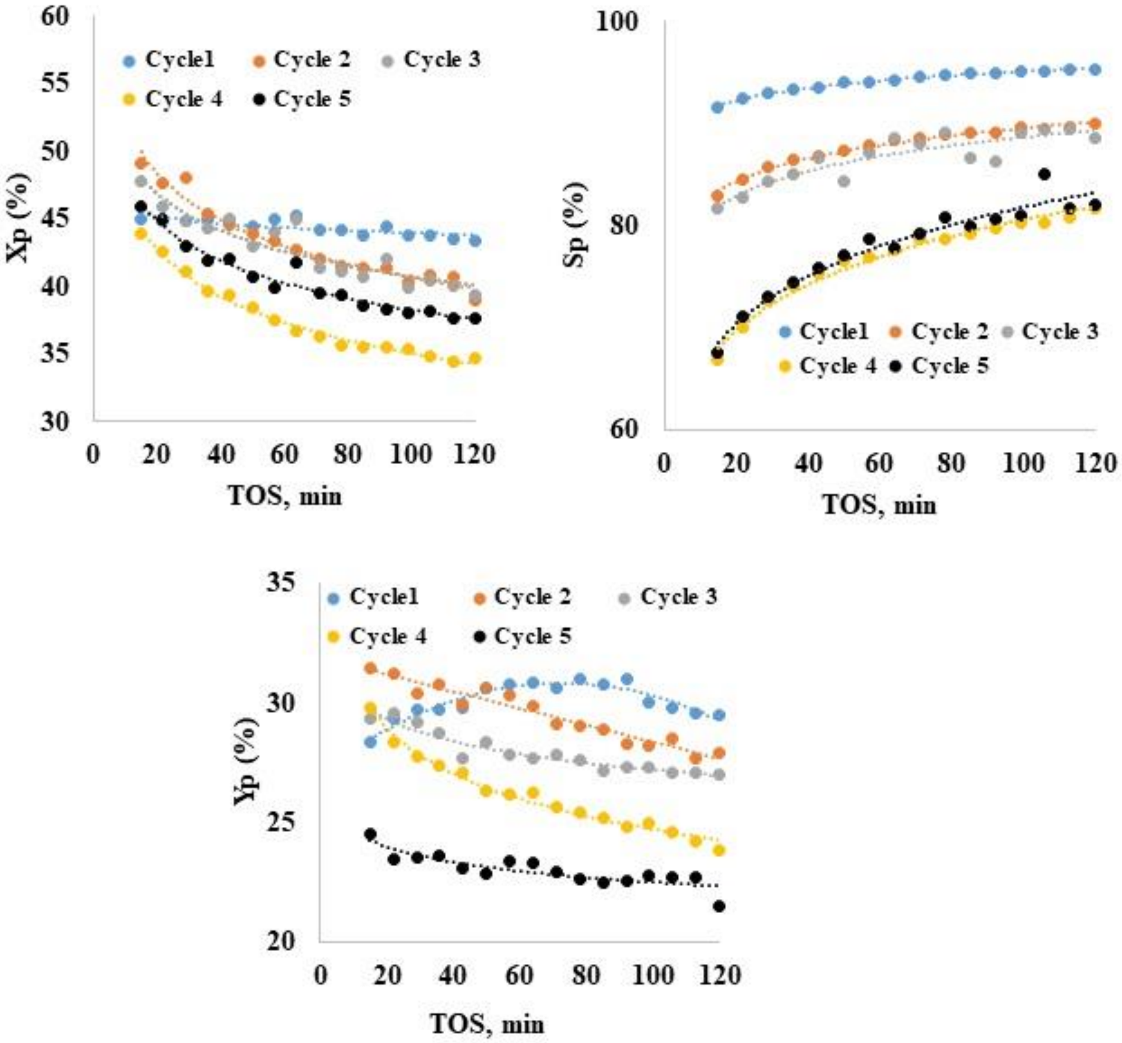

Fig. 6: Propane conversion (Xp), propylene selectivity (Sp) and propylene yield (Yp) at 575 °C, mola feed ratio of C_3H_8:H_2:N_2 = 1:0.5:5.5 and GHSV 3800h^{-1} for PtSnCa/γ-Al_2O_3 catalyst for five successive regeneration cycles.

Catalyst Regeneration

To estimate the stability as well as the propane dehydrogenation efficacy of the PtSnCa/γ-Al_2O_3 catalyst, regeneration studies were conducted for 5 successive cycles of catalyst deactivation and regenerations. The summary of obtained results is presented in Fig. 6.

In the first cycle, which is after 2h reaction time, the catalysts were regenerated at temperature of 575 °C in a mixture of 10 % oxygenand90 % nitrogen for three hours. For all subsequent cycles, the same catalyst sample was regenerated under similar conditions and all the catalytic activity evaluation tests were carried at the same reaction conditions.

The results showed a gradual decrease in overall % of propane conversion, and proportional decrease in propylene selectivity and yield. In comparison, the initial and final conversions were ~ 46.0% and 43.4 % respectively (during the first cycle) as to that of ~ 45.0 % and 37.6 % respectively for the fifth cycle. Similar variations were noted both in propylene selectivity and yield. After 5th cycle, the minimum propylene selectivity and its yield were 82% and 21% respectively. It indicates that catalyst was regenerated about~ 90% of its original activity of 46. 0 %. The remaining 10% loss in the activity of the catalyst after five regenerations may be attributed to loss of some active sites could be because of Pt nano particle's sintering which ultimately lead to their aggregation and hence decrease in number of Pt dispersion at the catalysts surface.

Catalyst stability studies

To assess the catalyst stability for long exposure of reactants to the catalysts,the catalytic experiment was carried for 50 hours continuously. The summary of propane conversion, propylene selectivity and yield are shown in Fig. 7.

Soon after beginning of the reaction, the propylene selectivity increased sharply up to 95 % and it remained within ±1% throughout the 50hours reaction time. However, a steady drop in both propane conversion and propylene yield, were noticed. It could be because of reaction under accumulated coke on the active sites of catalyst. At the end of 50 hours, propane conversion was still around 25 % with average yield of 29.6% - a clear indication of high resistance to rapid catalysts deactivation.

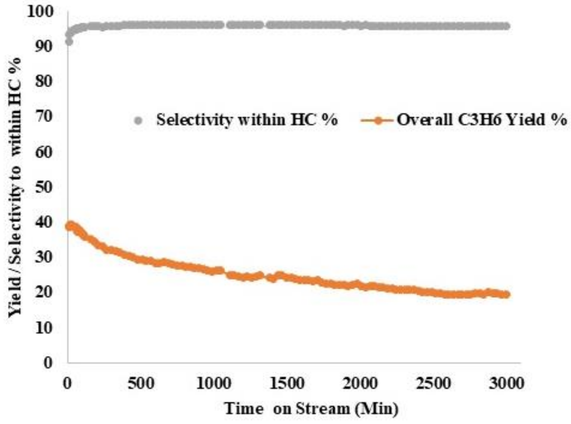

Fig. 7: Stability test of PtSnCa/γ-Al_2O_3 at 575 ºC, GHSV = 3800 h^{-1} and molar feed ratio of C_3H_8:H_2:N_2 =1:0.5:5.5

TPR Studies

To elucidate potential interaction of metals and support, a detailed TPR studies were performed for all the Ca containing catalysts and obtained results are shown in Fig. 8. Main reduction peak attributed to reduction of Pt oxide, for all "Ca" containing catalysts, appear at temperature range 289to 300 ºC. The second distinct peak, related to reduction of Sn species having strong interaction with Pt [36], appears at temperature range of 400 to 438ºC.

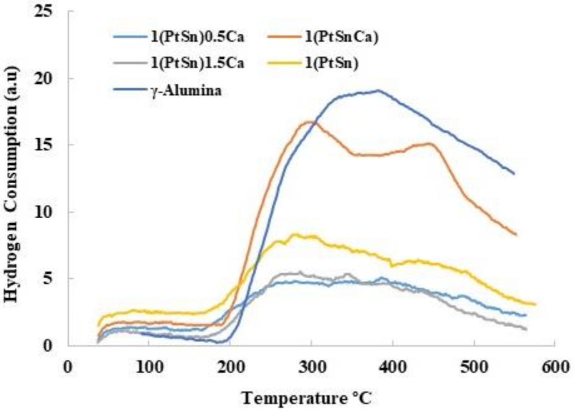

Fig8: H_2-TPR profile of four different calcium containing catalysts and support.

TPR data clearly shows that after "Ca" addition to PtSn/γ-Al_2O_3, peaks were shifted to higher temperatures, which implies that addition of Ca inhibits the reduction of Sn species - a beneficial factor for enhanced catalytic properties [37]. This means that upon "Ca" addition, most of the Sn species are converted to oxide. In Ca containing catalysts Sn was present as a Sn_2O_3 oxide, but not as a SnO_2 oxide. In bi-metallic Pt-Sn catalyst, state of Sn has pronounced effect on catalytic properties. Studies have shown that if Sn exists in the metallic state Sn^0, it acts as catalyst poison and when it exists as nonmetallic state (Sn^{+2} or Sn^{+4}) it acts as promoter[38]. The significant difference between the TPR profiles of four "Ca" containing catalysts exists due to "Ca" loading (Fig. 8). PtSn combination reduction profile shows a reduction peaks with maximum around the same temperature of 270ºC as the other catalysts but with lower peak intensity as to that obtained in $PtSnCa/\gamma\text{-}Al_2O_3$. This may be due to lower dispersion of Pt particles, which requires less hydrogen to reduce the surface Pt-O. The spectrum of this catalyst contains very small shoulder located at 465ºC. This may be due to reduction of Sn species, which interacts strongly with the support. Based on TPR results it was fair to conclude that calcium as promoter had positive effect in stabilizing the Sn species, which ultimately enhances the existing interaction of PtSn in $PtSn/\gamma\text{-}Al_2O_3$ catalyst.

Table 4: H_2 TPR peak temperatures of support and catalysts

Enrollment in local colleges, 2005

College	New students	Graduating students	Change
	Undergraduate		
Cedar University	110	103	+7
Elm College	223	214	+9
Maple Academy	197	120	+77
Pine College	134	121	+13
Oak Institute	202	210	-8
	Graduate		
Cedar University	24	20	+4
Elm College	43	53	-10
Maple Academy	3	11	-8
Pine College	9	4	+5
Oak Institute	53	52	+1
Total	998	908	90

Source: Fictitious data, for illustration purposes only

TPD of ammonia

Measurements of Temperature programmed desorption of ammonia was also carried for the support, the reference catalyst ($PtSn/\gamma\text{-}Al_2O_3$) as well as Ca containing catalysts to assess the effect of Ca addition on the surface acidity of the catalyst and its relation to catalyst performance in propane dehydrogenation. Obtained TPD profiles and data are shown in Fig. 9 and Table-5.

Obtained peaks of TPD are classified as follows:

i. The first low temperature peak, which is intense and relatively sharp was registeredat temperatures between 100and 270ºC. The maximum of this peak lies between 166and 208ºC depending on the calcium content.(Table-5). This TPD peak corresponds to ammonia desorption from weak acidic sites.

ii. The second less intensive and less resolved shoulder peak was registered at temperature around 300ºC;

iii. The third peak, which is of low intensity and quite broad was registered between 450 to 600 ºC with peaks maxim are gistered between 488 to 503ºC depending on catalyst composition. It represents the ammonia desorption from strong acidic sites (Table-5).

Referring to the first peak (see Fig. 9 and Table-5), it was very clear that the addition of Ca greatly influences the surface acidity and causes a shift in the peak maxima depending on calcium content. For the alumina support, the maxima of the 1stpeakwereregisteredat166ºC; where as it was shifted to higher temperature (208ºC) for the base catalyst ($PtSn/\gamma\text{-}Al_2O_3$). This was an indication of the transformation of weak acidic sites present on the alumina support to a relatively strong site present in Pt containing catalyst supported on alumina. In general, the acidic strength of these sites plays a vital role in determining the catalyst performance and thus the fine tuning of these acidic sites by addition of a basic agent such as calcium is very useful. In fact, as it was clear (see Fig. 9 and Table 5) that upon the addition of different proportions of calcium to the base catalyst ($PtSn/\gamma\text{-}Al_2O_3$) causes shifts in the position of the first peak. First peak – with an optimum calcium content of 1% that gives a maximum yield (32.1%) and selectivity (95.2%). This calcium content seems to produce an optimal surface acidity. A catalyst with zero calcium content possessestoo strong acidic sites (see first peak at 208ºCwhereas the catalyst 1% "Ca" gives the optimal acidic strength (1st peak at 178ºC) which ultimately lead to the best performance compared to other "Ca" containing catalysts.

The desorption peaks between temperature 350 and 600ºC are considered as a result of the presence of medium to strong acidic sites [39] similar to the peaks of support ($\gamma\text{-}Al_2O_3$) itself. Addition of "Ca"to the reference catalyst $PtSn/\gamma\text{-}Al_2O_3$, shifted the ammonia desorption temperature of strong acidic sites towards lower range – an indication that acid intensity becomes weaker on "Ca" addition. This effect was more profound in case of $PtSn1.5Ca/\gamma\text{-}Al_2O_3$. Hence, the decrease in acidic character of the support upon "Ca" addition was responsible for the enhanced stability of the catalyst by inhibiting the acid sites where the formation of coke take place.

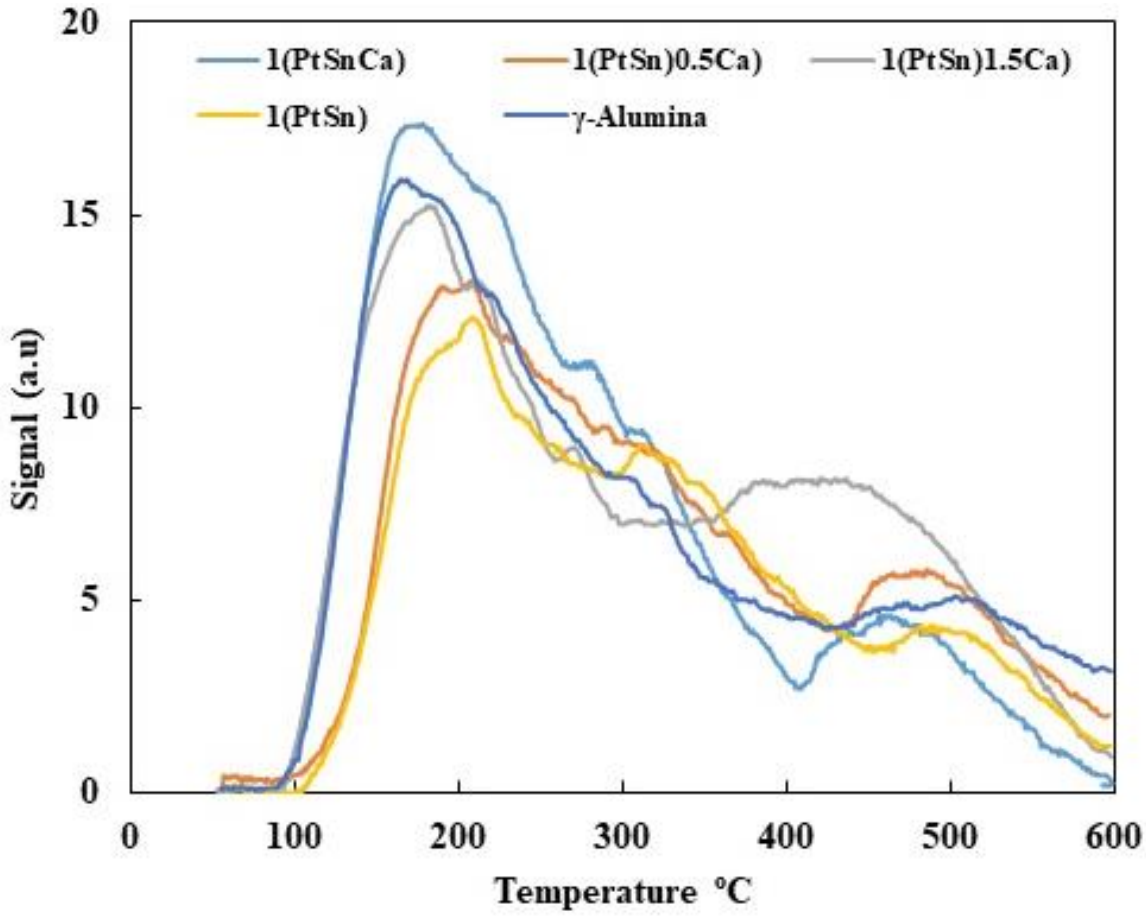

Fig. 9: NH$_3$ - TPD profile of four different calcium containing catalysts and support.

Table-5: NH$_3$ Desorption peak temperatures of support and catalysts

Enrollment in local colleges, 2005

College	New students	Graduating students	Change
	Undergraduate		
Cedar University	**110**	**103**	**+7**
Elm College	**223**	**214**	**+9**
Maple Academy	**197**	**120**	**+77**
Pine College	**134**	**121**	**+13**
Oak Institute	**202**	**210**	**-8**
	Graduate		
Cedar University	**24**	**20**	**+4**
Elm College	**43**	**53**	**-10**
Maple Academy	**3**	**11**	**-8**
Pine College	**9**	**4**	**+5**
Oak Institute	**53**	**52**	**+1**
Total	**998**	**908**	**90**

Source: **Fictitious data, for illustration purposes only**

CO Chemisorption Analysis

To investigate the extent of Pt dispersion, and its role in overall catalytic performance ofCa containing catalyst, a detailed CO chemisorption studies was conducted and obtained results are summarised in Table-6.

Table-6: Pt dispersion results from CO chemisorption for various catalysts

Enrollment in local colleges, 2005

College	New students	Graduating students	Change
	Undergraduate		
Cedar University	**110**	**103**	**+7**
Elm College	**223**	**214**	**+9**
Maple Academy	**197**	**120**	**+77**
Pine College	**134**	**121**	**+13**
Oak Institute	**202**	**210**	**-8**
	Graduate		
Cedar University	**24**	**20**	**+4**
Elm College	**43**	**53**	**-10**
Maple Academy	**3**	**11**	**-8**
Pine College	**9**	**4**	**+5**
Oak Institute	**53**	**52**	**+1**
Total	**998**	**908**	**90**

Source: Fictitious data, for illustration purposes only
*(used for 50 h; regenerated)

In general, a very high Pt dispersionisdetectedin almost all the Ca containing catalysts. The highly active catalyst PtSnCa/γ-Al$_2$O$_3$ has highest Pt dispersion. The average size of Pt metal crystallitesis in the range of 0.019 to 0.028 Å. A significant decrease in Pt dispersion and increase its crystal size is noticed after the extended use of the

PtSnCa/γ-Al_2O_3 catalyst. A clear indication of agglomeration of active metal content at the catalyst surface. Hence, PtSnCa/γ-Al_2O_3 had shown highest catalytic propylene conversion and propylene selectivity due to better Pt dispersion as well as enhanced catalytic stability due to the presence of Ca.

XPS studies

The active metal ionic state and/or possible impact of active metal surface concentration was estimated by having a detailed XPS analysis of fresh and used Ca containing catalyst PtSnCa/γ-Al_2O_3 (see Fig 10).

The active metal content of Pt was $Pt4d_{5/2}$ and $Pt4p_{5/2}$ (binding energy 350eV and 600eV respectively) having oxidation states of +4, +2 and +1. The Sn was in the form +2 with $Sn3d_{5/2}$ and $Sn3p_{5/2}$ (binding energy 489eV and 717eV respectively) and Ca exist in the form +2 with Ca_{2p} (binding energy 348 eV). The active metal content of Al was Al_{2p} with oxidation states of +3 and +1.

Impact ofAEE Properties on the catalytic activity and selectivity of the catalysts

To elucidate,which is the best AEE promoter, to PtSnZn/γ-Al_2O_3system,it was attempted to find a relation the betweentheAEEphysical properties [such as atomic number, melting points (MP) and densities (D)] and the catalyst properties [such as X_p , S_p, Y_p , Pt dispersion, and catalyst stability $Y_{p(stab)}$]. The summary of the results is shown in Figs. 11A-B. The values of all these physical properties and parameters for each promoted catalystwere plotted on y-axis in arbitrary units. On x-axis, promoted catalysts are plotted according to the gradual increase of the atomic number of AEE (used promoter).

In general, the chemical and physical properties of AEE changed gradually with the increase of the atomic number of the element. Interestingly, the "Ca" in comparison to other AEE, has highest M.P and minimal D. The catalytic activity results such as propane conversion (X_p), propylene selectivity (S_p), propylene yield (Y_p), Pt dispersion and catalyst stability $Y_{p(stab)}$,follows the same pattern as to that of M.P curve of all the AEE. In addition, coke formed during the catalytic reaction almost follows the same pattern as to that of D curve of almost all the AEE. This clearly indicates that the catalytic activity efficiency parameters [such as X_p , S_p, Y_p , Pt dispersion, and catalyst stability $Y_{p(stab)}$] has maximal values for the catalyst promoted by "Ca" with least amount of formed coke.Since "Ca" has least density among studied AEE and catalyst containing "Ca" exhibited least coking and higher catalyst stability Therefore, a direct relationship exists between D and extent of formed coke on the catalyst containing AEE. In general, the amount of formed cokedepends on the density of AEE.

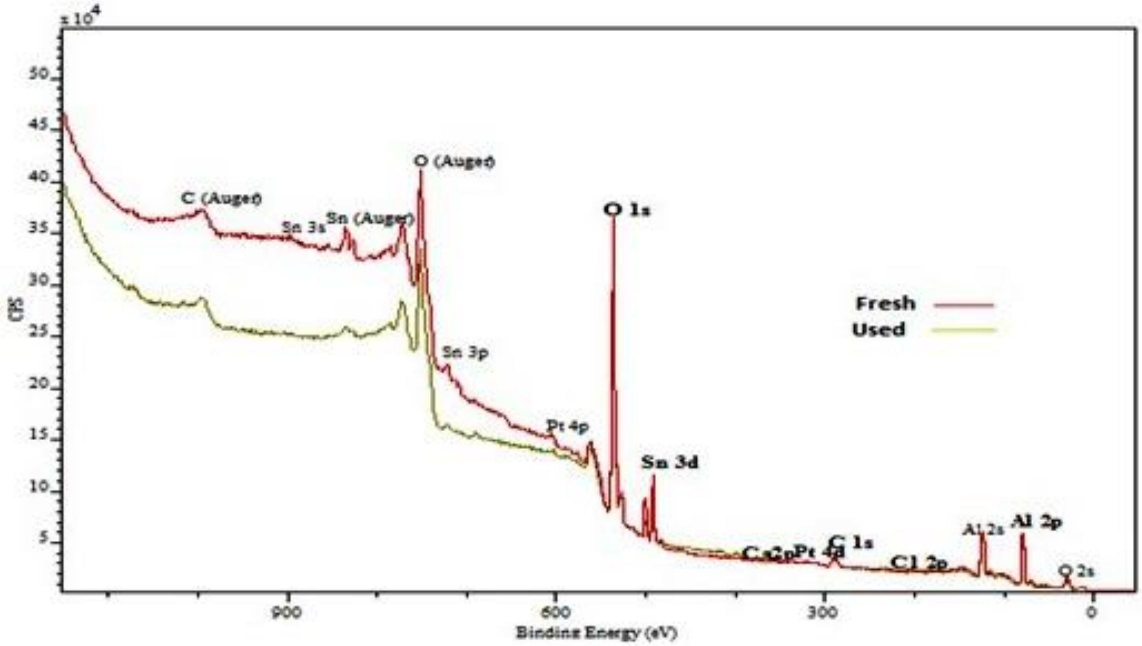

Fig. 10: XPS Spectra of fresh and de activated PtSnCa/γ-Al_2O_3 catalyst.

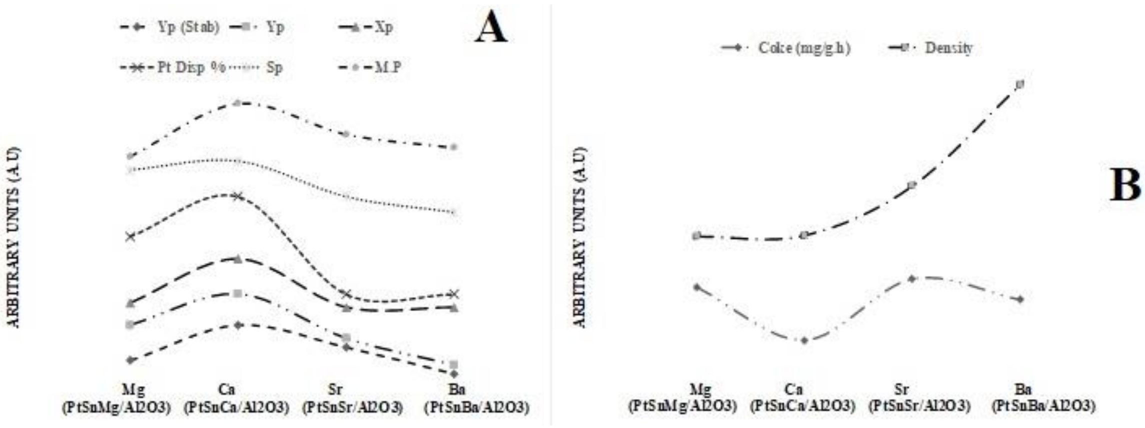

Fig. 11: Correlation of some AEE properties with catalytic properties of catalysts.

Also, it is proposed that because of melting point and density of AEE, “Ca” poses highest potential to be the best AEE promoter, which enhance the catalytic properties of Pt-Sn/γ-Al_2O_3 catalyst.

The addition of AEE, as promoters, decrease the acidity of the oxide support that lead to lower coke formation on the catalyst surface and enhances the catalyst stability. Positive effect of calcium addition to Pt-Sn/γ-Al_2O_3 in propane dehydrogenation reaction may also be attributed to increased thermal stability of the catalyst due to the formation of a protective layers between support and active metals particles, which inhibits the formation of inactive phases[40]. In addition, calcium interacts with the support itself and reduces the Pt-support interaction which, leads to better performance of the catalyst. Difference in the amount of coke deposited on the PtSn/γ-Al_2O_3 (19.9 $mg.g^{-1}.h^{-1}$) and PtSnCa/γ-Al_2O_3 (7.11 $mg.g^{-1}h^{-1}$), catalysts for longer reaction time, indicate that presence of “Ca” in the catalyst decreases the amount of the coke deposition on the active sites of platinum and it may have facilitated the rapid desorption of some of the coke precursors from metal surface.

As the calcium content of the catalyst was increased from 0.5 to 1.0 wt %, improvement in catalytic characteristics is observed. However, further addition of calcium (1.5 wt %) resulted in reduced activity of the catalyst. This was mainly because of increased Pt dispersion (from 44.2 % for 0.5% Ca to 52.5 % for 1.0% Ca), but it reduced to 42 % when Ca was further increased to 1.5 wt %. It indicates that adding calcium in excessive amount covers the support surface and may have blocked some of the pores due to the fact that surface coverage and blockage occurs preferentially in smaller pores[41].

It was well known fact, that acidic sites located on the Pt-Sn/γ-Al_2O_3 catalyst surface, during the propane dehydrogenation, promoteside reactions such as hydrocracking, isomerization and coke formation. NH_3-TPD profiles indicated that addition of Ca resulted in blockage of strong acidic sites leaving the medium or weak sites and hence diminish the overall acidic character of catalyst. By using excess HCl during the catalyst preparation, impregnation of active metals mainly decreases the Bronsted acidity of the sample.

In parallel, the addition of “Ca" may also have reduced the acidity of γ-Al_2O_3 because of the anchoring of“Ca”on the Lewis acid sites of Al^{3+}[42]. It was also reported that penta-coordinated Al^{3+} centers are bonding sites for Pt on γ-Al_2O_3 because of their strong interaction with atomic platinum and/or platinum oxide[43-45]. This decrease in acidity contributed to increased catalyst stability and reduced coke formation and hence better performance on PtSnCa/γ-Al_2O_3catalyst.

The initial steps of the coking process start on Pt active centers where the coke precursors (olefins) are formed. These olefins are propylene, ethylene and might be acetylene, which however was not registered in the final products of the reaction. They are adsorbed reversibly on the Pt active centers and a major part of them migrated through gas phase to the alumina surface on existing acidic centers. Later, on these surface-cites, the processes of polymerization and formation of mono- and bicyclic compounds begins, which steadily kept losing hydrogen and finally were transformed into graphiticcoke. Considering the above-mentioned possible mechanism of coke formation, it become clear the role of "Ca" in decreasing of the rate of coke formation. Obviously, the presence of "Ca" strongly depresses the polymerization and cyclization of formed olefins. Coking of the catalysts by carbon ion mechanism is strongly depressed by presence of AEE. It could be because of the high working temperature of the propane dehydrogenation where coke deposition take palace on the surface of the catalytically inert materials due to the formation of gas phase of free radicals. This process was depressed by tightly filling the reaction zone of the catalytic reactor with inert materials.

To stabilize Pt nanoparticles on the carrier surface in Pt/γ-Al_2O_3 catalyst, it was necessary to add to the catalyst composition, a metal with low melting point. The positive effect of adding Sn (melting point of 232 ºC) and Pb (melting point of 328 ºC) to Pt catalyst was well established and as a result Pt-Sn/γ-Al_2O_3 catalysts were developed, which was successfully used in industry for many years in the process of gasoline reforming in temperature interval 490-530ºC. The addition of low melting point element "Sn" to the catalyst composition prevents the highly dispersed Pt particles from aggregation and easily forms Pt compounds like Pt_3Sn, whichisregarded by many authors asactive species in the gasoline reforming process. In general, In Pt-based alkane dehydrogenation catalysts, the promoters play two primary roles, i.e., improving the dispersion and stability of Pt catalysts by forming PtM alloy, and decreasing the acidity of Pt catalysts. The process of propane dehydrogenation over Pt-Sn catalyst was carried out at temperature interval of 600-650 ºC. These temperatures are much higher than the temperature, at which Pt-Sn catalyst was used in hydrocarbon reforming process. Therefore, to preserve the high catalytic properties of the Pt-Sn system, it was necessary to stabilize it by adding a new component with higher melting temperature. Calcium, which has the highest melting point between all AEE was optimal for purpose of stabilizing Pt-Sn system.

The positive effect of calcium addition to Pt-Sn/Al_2O_3 in propane dehydrogenation reaction is attributed to the increased thermal stability of the catalyst and active metal, which also inhibits the formation of inactive phases[40].Calcium may also interact with the support itself that can reduce the active metal-support interaction, hence contributing towards the better performance of the catalyst. As we already have mentioned the addition of "Ca" to Pt-Sn catalyst lead to the formation of Pt particles with highest dispersion and "Ca" containing Pt-Sn catalysts has shown the best catalytic properties.

Another positive effect of addition of AEE, in particular"Ca" to the catalyst composition, was the depressing of the process of coking. The lowest density of "Ca" permits its easier dispersion on catalyst surface and uniform redistribution due to surface diffusion. Also, because of "Ca" mild basic character and low density, it was preferably get adsorbed on stronger acid centers of γ-Al_2O_3 thus decreasing the coke formation. Another probable reason for the specific effect of "Ca" as an effective promoter was the solubility of AEE in Pt and ability to form solid solutions with them.

Presence of "Sn" in catalyst composition leads to increased activity and selectivity of the catalyst due to decrease in both electron densities on "Pt" and charge transfer from "Pt" to "Sn" and/or γ-Al_2O_3. In addition, the acceptor strength of γ-Al_2O_3get decreased. The electron transfer depends on the "Pt" particle size. The stronger transfers take place if"Pt" particles size was less than 2 nm. Metal "Pt" particles with size $\geq$ 2 nm have the same electron properties as massive metal; however, in particles smaller than 2 nm most of the properties differ from the properties of massive metal.

Temperature programmed reduction was a useful tool not only to know the metal support interaction, but one can also understand the possible interaction of metal and promoter. As shown in Fig. 8, peaks at low temperature (<300 °C) for all the catalysts are due to reduction of platinum oxide that interacted with γ-Al_2O_3 support. Peaks at higher temperatures correspond to combined reduction of Pt-Sn oxides or Pt-Ca species. All samples show almost complete reduction. TPR profiles indicate to some extent that calcium addition to reference catalyst composition alleviates the Pt/support interaction and improves the PtSnCa interaction, which was beneficial for improvement of catalytic properties of the catalyst.

CO chemisorption results showed that addition of calcium improved the Pt dispersion on catalyst. However, excessive amount of calcium deteriorated the dispersion. This rise and fall in Pt dispersion with addition of increased amount of calcium was follows the activity results of calcium containing catalysts. Presence of adequate quantity of calcium was very useful for the propane dehydrogenation because of reduced accumulation of coke on the catalyst during the reaction. This was evident from the "Pt" dispersion measurement in used catalysts (PtSn/γ-Al_2O_3) reduced to half after reaction as to that slight variation in PtSnCa/γ-Al_2O_3.

Based on overall catalytic performance, "Ca" containing catalysts follows, the catalytic activity was in the order of PtSnCa/γ-Al_2O_3> PtSn1.5Ca/γ-Al_2O_3> PtSn0.5Ca/γ-Al_2O_3. In comparison to studied AEE, the"Ca" found the best among with the following order Ca>Mg>Sr>Ba.

Another aspect of the enhanced catalytic ability of PtSnCa/γ-Al_2O_3 as to that of PtSn/γ-Al_2O_3 was the key role played by "Sn" in the presence of "Ca". In case of PtSn/γ-Al_2O_3, Sn mostly is present in the form of SnO_2 and under the influence of hydrogen and higher temperature it undergoes a partial reduction:

$Sn^{4+} \rightarrow Sn^0 + Sn^{2+}$

This process was promoted by presence of Cl in oxidative and reduced atmosphere. This fact was important for the process of Pt re-dispersion by reacting with Cl or Cl containing compounds. Whereas, in PtSnCa/γ-Al_2O_3, we found that most of "Sn" exists in the form of Sn_2O_3 phase which was attributed due to "Ca" affinity with other catalysts components. In addition, "Pt" existed in the form of PtSn, $PtCa_2$ and Pt_2Al, all of which were not present in PtSn/γ-Al_2O_3. Further details can be found in author's previous published data [46]. Most probably, it was "Ca" who promotes formation of such phases due to specific electronic properties.

Above discussions, elucidate enough evidence for the beneficial effect of "Ca" addition to thePtSn/Al_2O_3 in terms of activity, selectivity and stability.

Conclusions

In conclusion, the addition of AEE to PtSn/γ-Al_2O_3 through wet impregnation, enhanced the overall catalytic conversion, increased propylene yield and its selectivity for propane dehydrogenation. Addition of "Ca" is the best among the other studied AEE.The PtSnCa/γ-Al_2O_3 catalyst had shown an overall highest propane conversion (~55.8%) along with 95.7 % propene (C_3H_6) selectivity within obtained hydrocarbons with least coke formation of 7.11 mg.g^{-1}h^{-1}. The effect of different operating parameters like temperature, feed ratio of reactants and GHSV was studied and the most suitable operating conditions were 575°C, C_3H_8:H_2:N_2 = 1.0:0.5:5.5 and GHSV of 3800h^{-1}. Addition of optimum amount "Ca" increased catalytic performance due to favorable adjustment of the acidic sites in γ-Al_2O_3support and/or PtSn/γ-Al_2O_3 along with very good "Pt" dispersion in PtSnM_1/γ-Al_2O_3 catalysts. The increased overall catalytic performance of PtSnCa/γ-Al_2O_3 was due to reduced coking process by the prevention of the polymerization and formation of mono- and bicyclic compounds due to lack of irreversible adsorption of olefins at Pt active surface. Increased thermal stability of the PtSnCa/γ-Al_2O_3 was due to a protective layer between support (γ-Al_2O_3) and active metal which allows the formation of active PtSn, Pt_2Ca and Pt_2Al.

Acknowledgements

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