

Propane Dehydrogenation over Pt-Sn Supported on Magnesium Aluminate Material

Deepa Govindarajan, Debdut Roy

Abstract—Pt-Sn catalysts have been prepared using magnesium aluminate as a support with two different Mg/Al ratio. The supports/catalysts have been characterized by N₂-adsorption, XRD, and temperature programmed desorption of NH₃ and thermogravimetry analysis (TGA). The catalysts have been evaluated at 595 °C for the propane dehydrogenation reaction at 0.5 barg pressure using a feed containing pure propane with steam to hydrocarbon ratio of 1 mol/mol and weight hourly space velocity (WHSV) 0.9 h⁻¹. Chlorine quantification studies have been developed using Carbon-Hydrogen-Nitrogen-Sulphur (CHNS) analyzer. The dechlorinated catalyst with higher alumina content showed better performance (38-43% propane conversion, 91-94% propylene selectivity) in propane conversion and propylene selectivity than Pt-Sn-MG-AL-DC-1 (30-18% propane conversion, 83-90% propylene selectivity).

Keywords—Dehydrogenation, alumina, platinum-tin catalyst, dechlorination.

I. INTRODUCTION

THE catalytic dehydrogenation of propane is of increasing importance because of the growing demand for propylene. Indeed, propylene is an important raw material for the production of polypropylene, acrolein, polyacrylonitrile and acrylic acid. However, the reaction of propane dehydrogenation is an endothermic process that requires a relatively high temperature to obtain high yield of propene. Therefore, it is the key to develop the catalyst possessing high-activity, high-stability and high-selectivity since the deactivation of the catalyst due to coke formation is inevitable. [1]-[3]. Supported bimetallic platinum (Pt)-based catalysts are widely used in both reforming and dehydrogenation processes. The support composition for bimetallic catalysts influences the sintering of metal particles and the formation of coke on the support itself. It has been reported that non-acidic materials such as alkali-doped alumina, spinels, and calcined hydrotalcite could minimize the adsorption of alkene and the formation of coke. Previous studies have shown that the formation of coke is minimized using non-acidic supports such as K-L zeolite, alkali-doped alumina, spinels, and calcined hydrotalcite [Mg(Al)O] [4]-[9]. Out of these supports, MgAl₂O₄ (magnesium aluminate) has also attracted much attention as a catalyst support because of its interesting properties such as low acidity, high thermal resistance, good

hydrothermal stability and good interaction with the active species. Such materials are hydrothermally stable and are capable of dispersing small Pt particles due to the presence of Al cations at the support surface. The basic character of the support is also desirable, since it minimizes coke formation [10]-[13].

The use of chlorinated Pt precursors for dehydrogenation reaction has raised several issues because of residual chlorine. The residual chlorine also influences catalytic characteristics, including structural properties, acidity and available active sites. Removing chlorine from the catalysts impregnated in hydrochloric acid (HCl)-acidified aqueous solution proved important in obtaining stable performance [14]-[17]. The adverse effect of chlorine is most likely due to increased coke formation on acid sites. Chlorine features on Pt-based catalysts produced by the different treatments may result in variant behaviors that may significantly affect catalytic performance [15]. Paulis et al. [16] found that the mobility of chlorine is responsible for altered reaction stability of Pt/Al₂O₃ catalysts by systematically studying the effect of chlorine on the properties of these catalysts. Arteaga et al. [17] investigated the catalyst regeneration over Pt/Al₂O₃ and Pt-Sn/Al₂O₃ with and without chlorine in detail and concluded that the presence of both tin (Sn) and chlorine exerts additional effects on side reactions on reduced catalysts.

We now examine the activity of Pt (0.3 wt%) and Sn (0.6 wt%) supported on MgAl₂O₄ with two different Mg/Al ratios and effect of dechlorination for the MgAl₂O₄ support in propane dehydrogenation reaction. The catalysts and supports are characterized by many methods. A method has been developed for the quantification of chloride content in the catalysts. Attempts are made to rationalize the activity of the different catalysts based on the characterization data.

II. EXPERIMENTAL

A. Preparation of Support & Catalysts

MgAl₂O₄ supports in 3 mm extrudates form with different Mg/Al ratio (MG-AL-1 and MG-AL-2) were received from PIDC, USA. Pt and Sn were loaded on the above supports by a co-impregnation method using an aqueous solution of H₂PtCl₆.6H₂O (Hindustan Platinum (P) Ltd., India) and SnCl₂.2H₂O (Merck Specialties Pvt. Ltd., India). The required amounts of Pt and Sn compounds were dissolved in ethanol. The support extrudates were broken into small pieces (3 mm size; water-washed and dried) prior to loading of the metals. The impregnated samples were dried at room temperature for about 12 h in air. The air-dried samples kept for overnight at 100 °C and calcined for 4 h at 560 °C. The impregnated

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support is named as Pt-Sn-MG-AL.

B. Dechlorination Procedure

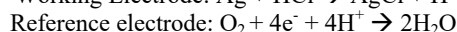
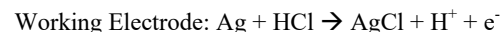
To dechlorinate the catalyst, 25 ml 0.5 M ammonia solution at a temperature between 40-70 °C was added to the Pt-Sn-MG-AL-1 & Pt-Sn-MG-AL-2 and the liquid was decanted after 5 min. The same procedure was repeated two more times. After ammonia treatment, the catalyst was washed with hot water for about 10 to 20 times to remove surface adsorbed ammonia. The hot water treated catalyst was air dried for 12 h followed by oven drying at 120 °C for about 6 h. The calcination was carried out at a temperature of 550 °C for 4 h at a ramp of 0.5 °C. These dechlorinated catalysts are named as Pt-Sn-MG-AL-DC-1 and Pt-Sn-MG-AL-DC-2.

C. Catalyst Characterization Techniques

Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP 2020) from N₂ adsorption data obtained at liquid N₂ temperature. Pore volumes and average pore size were obtained by the Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) patterns of the supports and catalysts were obtained using a Rigaku Miniflex II with Cu K alpha radiation in 0.5° ramp. The acidity of the catalysts were measured by the temperature programmed desorption (TPD) of NH₃ (AutoChem-II 2920, Micromeritics, USA). About 100 mg of sample was packed properly in a quartz tube. The sample was then degassed at 250 °C for 1 h under He stream (30 mL/min) afterwards cooled down to 50 °C; the degassed sample was saturated in an NH₃ stream (14.8% NH₃ in He) for 30 min with flow 30 mL/min. After that, the sample was purged with He (20 mL/min) at 50 °C for 30 min. to remove the physically adsorbed NH₃. The gas coming from the sample is analyzed directly by a thermal conductivity detector (TCD). The NH₃-TPD measurement was carried out with a temperature ramp of 10 °C min⁻¹ from 50 °C to 600 °C under a He stream (30 mL/min). The areas under the TPD curves were converted into milli.equiv. NH₃ desorbed per gram of catalyst based on injection of known volumes of the He-NH₃ mixture under similar conditions.

D. Method Development for Quantification of Chlorine

The measurement of chlorine is done using the traditional method of Schöninger digestion. The high temperature combustion using the elemental analyzer with a suitable detector to quantify the HCl gas produced during combustion has been followed. We followed similar principle and a method has been developed to quantify the chloride content using the CHNS analyzer. The principle adopted in the "Elementar CHNS analyzers" was by converting the chloride content in the sample to HCl by the use of high temperature combustion. The evolved HCl is then forwarded to the electro chemical cell by the use of compressed air as carrier gas, which is pre-dried with siccacide. From the detected amounts of HCl the chloride content is estimated. The working principle of the electro chemical cell is based on the following reaction:



The electrons in this reaction lower the current between working and the reference electrode; which is a measure for the HCl concentration in the carrier gas.

About 8-10 mg of powdered sample was taken in a tin boat (in duplicates); crimped well and loaded into the auto-sampler and further to which it was introduced into the Elementar elemental analyzers (Inst.Spec. Elementar Vario EL cube with Chloride attachment) at a combustion temperature of 1150 °C using a compressed air as a carrier gas for chloride quantification. The carrier gas flow rate was maintained at 300 mL/min using an electrochemical cell as a detector. The instrument was calibrated with 0.1 N HCl as standard. The estimation of chloride was validated by using known concentration of ICP grade chloride solution and its recovery was estimated [18].

E. Reaction Procedure

Propane dehydrogenation (PDH) was studied using the Pt-Sn-MG-AL catalysts in a low pressure fixed-bed inconel reactor (i.d. = 3/4 inch) operated in the down-flow mode. About 4 g of catalyst (2-3 mm in size) and 6 g of 0.35 mm particle size silicon carbide was used to prepare the catalyst bed. The reactor was heated under 2 °C/min ramp in N₂ at 500 °C and then the catalyst was reduced at 500 °C, under 2 SLPH flow of hydrogen (99% purity) for 1h. A PDH experiment started with the typical condition as shown in Table I. Analysis of the products is done by gas chromatography (Agilent Analytical GC – Model 6890; HP-Plot alumina-sulfate column for FID and Carboxen Plot 1010 for TCD).

TABLE I
FEED AND PROCESS CONDITIONS USED IN PDH REACTION

Catalyst	Feed	Process Conditions			
		T (°C)	P (bar)	WHS V (h ⁻¹)	SHC (mol/mol) @STP
Pt-Sn-MG-AL-1	Propane (99 wt%)	585	1.53	0.9	1
Pt-Sn-MG-AL-DC-1					
Pt-Sn-MG-AL-2					
Pt-Sn-MG-AL-DC-2					

Propane conversion and propylene selectivity are defined as follows:

$$\text{Conversion of propane} = \frac{(In_{\text{moles C}_3\text{H}_8/\text{hr}} - Out_{\text{moles C}_3\text{H}_8/\text{hr}})}{In_{\text{moles C}_3\text{H}_8/\text{hr}}}$$

$$\text{Selectivity to } i_{th} \text{ component} = \frac{Out_{\text{moles of } i/\text{hr}}}{(In_{\text{moles C}_3\text{H}_8/\text{hr}} - Out_{\text{moles C}_3\text{H}_8/\text{hr}})}$$

III. RESULT AND DISCUSSION

A. XRD

The XRD patterns for MG-AL-1 and MG-AL-2 supports, oxides and dechlorinated oxides samples are presented in Figs.

1 and 2. XRD analysis of the sample prepared by impregnation of the calcined hydrotalcite (with an ethanol solution) before the final calcination shows that the usual diffuse $\text{Mg}(\text{Al})\text{O}$ pattern is retained. This result indicates that no major structural changes take place during impregnation in ethanol. The XRD patterns show MgO as the only crystalline phase. However, the diffuse peaks indicate that the material has a relatively high defect density. Since, the $\gamma\text{-Al}_2\text{O}_3$ phase crystallizes in the same spinel structure as MgAl_2O_4 phase, the little crystals of $\gamma\text{-Al}_2\text{O}_3$ present in excess on both the samples

were not observed by XRD.

In Figs. 1 & 2, it can be seen that there is an increase on the broadening of all the diffraction peaks, indicating a decrease in crystallite size of the MgAl_2O_4 phase as the Al/Mg atomic ratio increases. In the MG-AL-2 sample (MgAl_2O_4), the highest degree of crystallization was observed. Therefore, the $\gamma\text{-Al}_2\text{O}_3$ present in the support retards the sintering process of small crystals of MgAl_2O_4 . In this sense, the $\gamma\text{-Al}_2\text{O}_3$, although it contributes to support surface area, also favors to increase the specific surface area of MgAl_2O_4 [19].

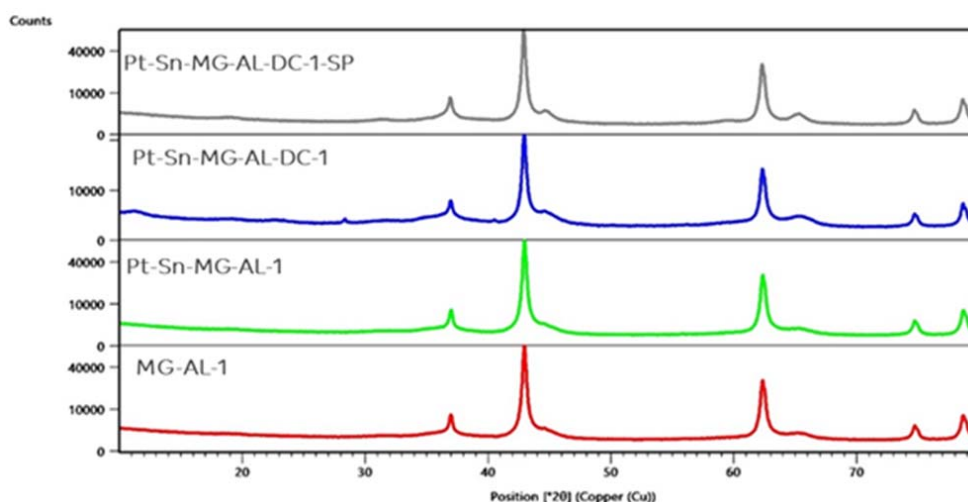


Fig. 1 XRD patterns for the MG-AL-1 support and catalyst

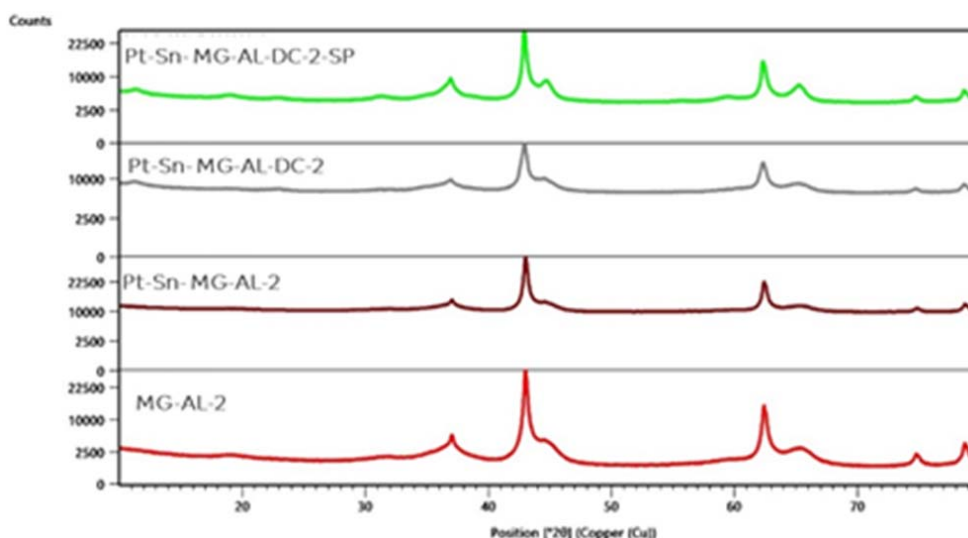


Fig. 2 XRD patterns for the MG-AL-2 support and catalyst

B. Textural Properties

The surface area of the MgAl_2O_4 support increased dramatically with increase in aluminum content. There are two possibilities during the blending of alumina with MgAl_2O_4 support: Inside the MgAl_2O_4 spinel structure, alumina may occupy the octahedral vacancies to form a non-stoichiometric

MgAl_2O_4 (in the MgAl_2O_4 normal spinel structure), only 1/8 of the octahedral sites are occupied [20], or alumina may segregate from the MgAl_2O_4 spinel structure and present as an extra $\gamma\text{-Al}_2\text{O}_3$ phase. In the latter case, $\text{MgAl}_2\text{O}_4\text{-}\gamma\text{-Al}_2\text{O}_3$ mixed support would be formed. The role of $\gamma\text{-Al}_2\text{O}_3$ was to retard the sintering of MgAl_2O_4 crystals, which increases the surface area of MgAl_2O_4 . Hence, the Pt-Sn-MG-AL-2 (130

m²/g) has higher surface area than Pt-Sn-MG-AL-1 (97 m²/gm). The pore volume for the Pt-Sn-MG-AL-2 catalyst samples were in the range of 0.4 to 0.5 cm³/g. Since primary spinel crystal itself is a non-porous material, the sample pore originates from the stacking of primary particles. [21] It is observed that the dechlorination and the increase in alumina content enhance the drop in surface area of the Pt-Sn-MG-AL-2 samples. From this analysis, it is clear that the aluminum concentration has a great influence on the textural properties of supports along with the chlorine treatment.

TABLE II
TEXTURAL PROPERTIES OF SUPPORTS AND DECHLORINATED CATALYSTS

Sample Code	S _{BET} ^a , m ² /g	PV _{total} , cm ³ /g	Pore size, Å
MG-AL-1	93	0.43	161
Pt-Sn-MG-AL-1	97	0.43	182
Pt-Sn-MG-AL-DC-1	95	0.38	132
MG-AL-2	130	0.54	154
Pt-Sn-MG-AL-2	120	0.5	156
Pt-Sn-MG-AL-DC-2	109	0.43	148

^aSurface areas calculated by the BET method. N₂ (liq) sorbed at p/p₀ = 0.99.

C. Acidity Characteristics

The TPD profiles of the supports and the catalysts (oxide state and dechlorinated state) are presented in Fig. 3. The acidity values obtained from the TPD profiles of both the supports and catalysts are presented in Table IV. While the total acidity of the sample is given by the area under the TPD curves, an idea of the distribution of acidity in the sample may be obtained from the amount of NH₃ desorbed at different temperatures, the temperature of desorption being directly related to the strength of the acid sites.

There are two distinct temperature peaks in the temperature range 50-250 °C and 250-500 °C. These two peaks represent two different types of acidic strength, i.e., weak and moderate-strong site acidity [22]-[24]. The first peak with maxima around 100 °C is the low temperature peak (l-peak) which is attributed to the desorption of weakly bound ammonia. The

second peak, with maxima around 300 °C is called the high temperature peak (h-peak) and it is usually attributed to the moderate to strong or strong acid sites (ammonia desorption from the Brønsted acid sites) [22], [25], [26]. The acidity of the MG-AL-1 and MG-AL-2 supports was 0.16 and 0.30 mmol/gm. With increasing Al content, as expected the acidity is increased for the supports. The TPD acidity values for the Pt-Sn-MG-AL-2 support, oxide and dechlorinated samples are in the range of 0.30 to 0.59 mmol/g. These features clearly show that the increase of acidity in the samples is correlated with the γ-Al₂O₃ concentration in the supports. However, the alumina content was 10% higher than Pt-Sn-MG-AL-1 sample.

Generally, the acidity of the samples will decrease after removal of chloride from the catalysts. However, in both catalysts Pt-Sn-MG-AL-1 & Pt-Sn-MG-AL-2, the acidity increased in both weak and strong acid sites after dechlorination. Especially in Pt-Sn-MG-AL-1, the acidity in the temperature range of 100 °C increased from 0.10 mmol/g to 0.19 mmol/g after dechlorination. However, in the case of Pt-Sn-MG-AL-2 samples' weak acidity decreased from 0.15 mmol/g to 0.11 mmol/g and strong acid sites is increased from 0.15 mmol/g to 0.45 mmol/g.

TABLE III
ACIDITY CHARACTERISTICS OF SUPPORTS AND CATALYSTS

Catalyst	Acidity				
	Support		Total	Oxide	Dechlorinated Oxide
	<100 °C	~350 °C			
MG-AL-1	0.1	0.06	0.16	0.43	161
MG-AL-2	0.15	0.15	0.3	0.43	148

The overall acidity of the dechlorinated catalyst increased from 0.29 mmol/g to 0.56 mmol/g for Pt-Sn-MG-AL-DC-2. Arteaga et al. also found that the presence of chlorine could increase the acidity of the support [27]. Introduction of chlorine is an essential approach to acidify the support surface and promote Pt dispersion in many industrial reforming catalysts [28].

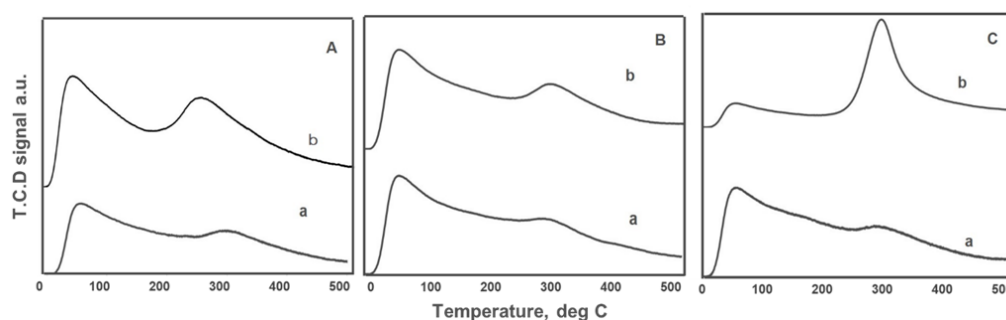


Fig. 3 TPD (of NH₃) curves of (A): supports, (B): oxide catalysts and (C): dechlorinated catalysts. (a) MG-AL-1, (b) MG-AL-2

Sachtler [29] also assumed the formation of a surface complex from a promoter, support, and chloride that could alter the acidic function of the catalyst. Therefore, chlorine elimination treatment in reverse also significantly affects multiple characteristics of the catalysts, the type of Pt active

phases, even the behavior of hydrocarbon reconstruction. Though the acidity of the Pt-Sn-MG-AL-DC-2 sample was higher, it shows better activity compared to the other catalysts.

D. Chloride Quantification

The chloride content in the dechlorinated and non-dechlorinated samples was compared in Table IV. The following observations have been made: the chloride content in the non-dechlorinated samples for both Pt-Sn-MG-AL-1 and Pt-Sn-MG-AL-2 ranged from 0.37% to 0.43% and for the dechlorinated catalyst samples Pt-Sn-MG-AL-DC-1 and Pt-Sn-MG-AL-DC-2, it was found to be in the range of 0.2% to 0.4%. The overall reduction in the chloride content ranged from 5.59% to 25%. The lowest chloride content was observed in the sample of Pt-Sn-MG-AL-DC-2 (0.28%).

The method adopted for the quantification of chloride looks to be in line with process expectation; where in the dechlorinated sample, it is always relatively lower in chloride content in comparison to that of the non-dechlorinated sample.

The validation studies conducted with known concentration of Cl solution (1000 ppm-ICP grade reference standard) showed acceptable recoveries ranging from 92% to 95%.

TABLE IV
CHLORIDE QUANTIFICATION

Sample code	Chloride content (% wt/wt)	% Relative reduction in Chloride content
Pt-Sn-MG-AL-1	0.43	Not applicable
Pt-Sn-MG-AL-2	0.38	Not applicable
Pt-Sn-MG-AL-DC-1	0.41	5.6
Pt-Sn-MG-AL-DC-2	0.28	25.6

IV. PDH

Dehydrogenation reaction over two different catalysts prepared using MgAl_2O_4 and alumina blended supports are reported in this section. The MG-AL is impregnated with Pt-Sn metals followed by dechlorination treatment. The reactions were tested with dechlorinated and non-dechlorinated catalysts at different dehydrogenation reaction conditions.

A. Performance of Pt-Sn-MG-AL-1 Catalyst

The catalyst performance results for fresh and regenerated Pt-Sn-MG-AL-1 catalysts are compared in Fig. 4. The catalyst after a reaction of 8 h was regenerated under 35 ml/min air flow at 525 °C for 2 h. The third cycle data for Pt-Sn-MG-AL-1 show better selectivity compared to fresh catalyst. The conversion for the fresh catalyst was around 49% and there is a decrease in the conversion for the regenerated catalyst in the third cycle (40%). It was found that the propylene selectivity was enhanced compared to fresh catalyst in the regenerated catalyst (increased from 70% to 84%). The key role of dehydrogenation catalysts is to accelerate the main reaction and control other reactions. Unmodified alumina-supported Pt catalysts are highly active but are not selective to dehydrogenation. [30]

The reaction was performed at high steam to propane ratio of 2.7 mole/mole, hence in Pt-Sn-MG-AL-1 fresh and regenerated catalysts, CO_2 (9 to 11 mol%) formation is higher w.r.t steam to hydrocarbon ratio. In the regenerated catalysts, as the conversion drops down from 49% to 40%, the selectivity increased from 70% to 84%. However, the side products formed in both fresh and regenerated catalysts are

similar. If we consider methane and ethane formation, they are in the range of 2 to 4 mol% in both fresh and regenerated catalysts. When steam is used, MgAl_2O_4 increases its catalytic activity, but propane conversion remains very low. Selectivity varies as a function of conversion for a given set of operational variables.

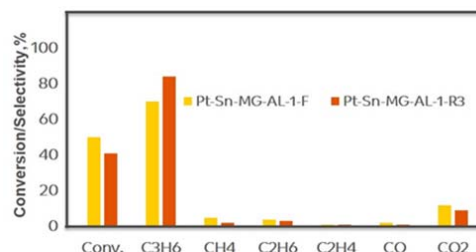


Fig. 4 Conversion of propane and product distribution over Pt-Sn-MG-AL-1 fresh (F) and regenerated (R3) catalysts. Reaction Conditions: Temp = 585 °C, WHSV = 0.9 h⁻¹, Steam/C₃H₈ = 2.7 mol/mol, Pressure = 0.5 barg, F-fresh, R3-third regeneration cycle

B. Performance of Dechlorinated Catalysts

The dechlorinated catalysts pretreated and regenerated at similar conditions as in Pt-Sn-MG-AL-1 catalyst. Subsequently, the reactor temperature, pressure, propane and steam flow rate were adjusted to the required values as mentioned in Table I to start dehydrogenation reaction. The catalyst performance results for fresh and regenerated catalysts are compared in Figs. 5 and 6.

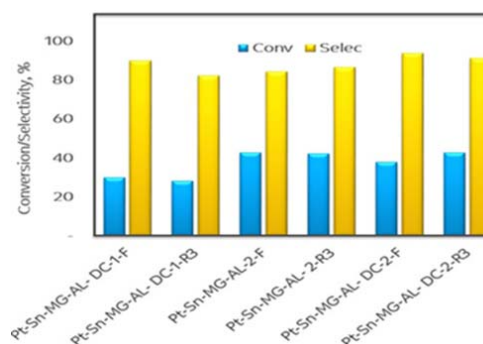


Fig. 5 Conversion of propane and selectivity over different for fresh and regenerated catalysts. Reaction Conditions: Temp = 585 °C, WHSV = 0.9 h⁻¹, Steam/C₃H₈ = 1 mol/mol, Pressure = 0.5 barg, F-fresh, R3-third regeneration cycle

The conversion drop was observed with Pt-Sn-MG-AL-DC-1 from fresh (30%) to regenerated catalyst (27%). The selectivity was also reduced from 90% to 82%. It was found that the chloride removal was less compared to the Pt-Sn-MG-AL-DC-2 catalyst from the chloride analysis. After dechlorination, formation of CO & CO₂ are less. The cracking products are also less compared to the catalyst without dechlorination. The CO₂ formation was around 2% in dechlorinated sample, whereas, the CO₂ was around 4% in the non-dechlorinated catalyst which enhances the selectivity of propylene. In the case of non-dechlorinated sample, the

conversion is more but the selectivity is less. After dechlorination, the conversion drops down by ~5%, but the propylene selectivity increases to almost from 69% to 90% for the fresh catalyst of non-dechlorinated and dechlorinated of Pt-Sn-MG-AL-1 catalysts.

When steam is used, MgAl_2O_4 increases its catalytic activity, but propane conversion remains very low. Selectivity varies as a function of conversion for a given set of operational variables. The chlorine-rich catalyst deactivates significantly in terms of initial activity, presumably because of increased coking on acidic sites. Hence, a higher chlorine content clearly reduces the lifetime stability of the catalyst. Metal deposition onto the (uncalcined) hydrotalcite and a low chlorine content on the final catalyst lead to enhanced performance compared to the initial preparation procedure. [31] However, chlorine is known to increase the acidity of the support, which can lead to increased coking and, in turn, render the catalyst more difficult to regenerate. Therefore, measures had to be taken to reduce the chlorine content of the catalysts after impregnation.

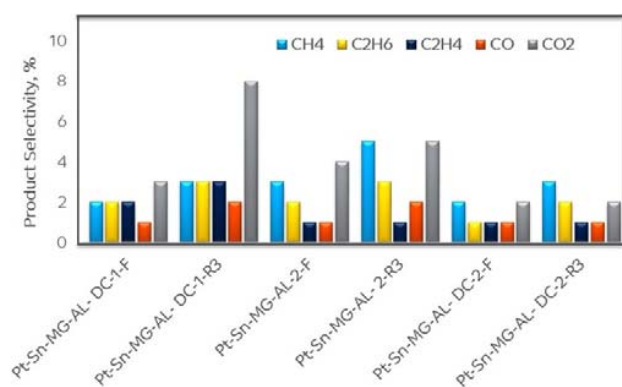


Fig. 6 Product distribution over different for fresh and regenerated catalysts: Reaction Conditions: Temp = 585 °C, WHSV = 0.9 h⁻¹, Steam/C₃H₈ = 1 mol/mol, Pressure = 0.5 barg, F- fresh, R3- third regeneration cycle

In the case of Pt-Sn-MG-AL-2, significant catalyst improvement in propylene selectivity is observed (84.3% and 86.7% for Pt-Sn-MG-AL-2-F and Pt-Sn-MG-AL-2-R3 to 93.9% and 91.3% for Pt-Sn-MG-AL-DC-2-F and Pt-Sn-MG-AL-DC-2-R3 respectively).

Noting that steam would further induce changes of Pt-Sn structure that tin would segregate from Pt-Sn particles to expose more Pt active sites or sinter Pt particle, depending on contacting time. The exposure of more Pt active sites would also partly account for the recovered activity and the low propene selectivity observed at the beginning of each dehydrogenation process. [32], [33] The effect of oxygenate additives on the performance of Pt-Sn based catalyst in the PDH process, supposed that the surface hydroxyl might also be involved in the dehydrogenation steps and thus lowering the overall activation energies and subsequently promoting dehydrogenation rates. In accompany with the decomposition

of original Pt-Sn alloys, more accessible Pt sites would be generated and increase the catalytic activities. [34] This improvement in propylene selectivity without effecting propane conversion is attributed to the dechlorination effect to the catalyst. There are indications that the initial behavior during the first cycles might be related to the amount of Pt in the catalyst. Zinc and MgAl_2O_4 are neutral or slightly basic and therefore do not need alkaline promoters; alumina supports, on the other hand, they need alkaline promoters to minimize the acidic properties of the system responsible for a decrease in the selectivity and life of the catalyst. The main role of the support consists in stabilizing the dispersion of the Pt, especially during the regeneration of the catalyst, by means of the combustion of the coke. While Pt deposits on silica sinters following oxidative treatments, the sintering is very limited for Pt on alumina and practically absent for Pt supported on MgAl_2O_4 , even after many regeneration cycles.

In the non dechlorinated catalysts, the methane formation is around 5% in Pt-Sn-MG-AL-2, which is due to more aluminum in the Pt-Sn-MG-AL-2 sample, which leads to cracking because of the acid sites. If we compare the ethane and ethylene formation, the ethane formation is around 2-3% where ethylene is ~1%. This shows that the aluminum content prefers more towards methane and ethane formation compared to dehydrogenation reaction. In Pt-Sn-MG-AL-1 sample, the CO₂ formation was around ~10%, and propylene selectivity is ~78%. Generally, the Pt supported system is more active for dehydrogenation. In order to suppress this, the Pt is alloyed with some other metals like tin, gallium etc. During regeneration with steam, the Pt-Sn alloy formed will disintegrate and Pt will be free for dehydrogenation process. The regeneration with steam may migrate the alloy formed with Pt so that the dehydrogenation increases due to Pt. This might be one of the reasons for the increase in conversion after regeneration.

If we study the Mg/Al ratio effect, the optimum ratio was found to be Pt-Sn-MG-AL-2 sample since the conversion and selectivity are 42% & 92%. However, in Pt-Sn-MG-AL-1 sample, conversion is more compared to selectivity. This might be due to the presence of more alumina content in the hydrotalcite structure, which paves the way to form the active sites for the reaction [35]. Thus, an increase in the magnesium content in the support leads to two main aspects: i. increase in the support's basicity, ii. weakening the interaction of the anionic precursors with Pt. [36] As a consequence, the dispersion of Pt in the finished catalyst may decrease with an increasing Mg/Al ratio. In addition, it was established that the reduction of the Pt outer sphere complexes diminishes the proportion of oxidized Pt species in the finished catalyst [37], [38]. The higher the surface area, higher the dispersion of the metal species in Pt-Sn-MG-AL-2 leading to the better performance in the PDH reaction. The acidity of the better performing catalysts is more but still the formation of side products is lesser compared to Pt-Sn-MG-AL-DC-1 catalyst at similar reaction conditions.

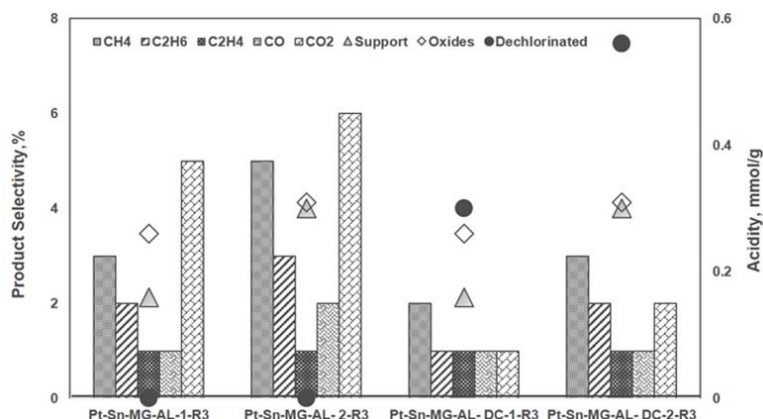


Fig. 7 Relationship between acidity (TPD) of catalysts and supports and PDH reaction: For: Pt-Sn-MG-AL-DC-1, Pt-Sn-MG-AL-2 & Pt-Sn-MG-AL-DC-2: Reaction condition: Catalyst: 4 g; WHSV: 0.9 h⁻¹; S/HC: 1:1 mol/mol; Temp.: 585 °C; Pressure: 0.5 barg. For Pt-Sn-MG-AL-1: Catalyst: 4 g; WHSV: 0.9 h⁻¹; Temp.: 585 °C; Pressure: 0.5 barg S/HC: 2.5 mol/mol; 3rd cycle result

The conversion, selectivity and yield of propylene for the third cycle data are plotted in Fig. 7. It shows that the Pt-Sn-MG-AL-DC-2 performs better than the other catalyst. Fig. 7 shows the total acidity and side products formed during the PDH for the four catalysts in the third cycle data. The total acidity was higher for Pt-Sn-MG-AL-DC-2, around 0.56 mmol/gm, but the side products are less. It has been explained that though after dechlorination, the acidity might increase which also enhances the propane conversion and propylene selectivity. If we compare the Pt-Sn-MG-AL-1 and Pt-Sn-MG-AL-DC-1, the formation of CO₂ is drastically reduced from 4% to 1.5%. However, in the case of Pt-Sn-MG-AL-DC-2 & Pt-Sn-MG-AL-DC-2, though the acidity is lesser in Pt-Sn-MG-AL-2, the formation of CO₂ and methane formation are comparable with the dechlorinated sample.

The catalyst can be arranged in the following decreasing order of conversion and selectivity for the fresh non-dechlorinated and dechlorinated catalysts:

Conversion:

- **Fresh:** Pt-Sn-MG-AL-1 > Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-DC-2 ~ Pt-Sn-MG-AL-2
- **Regenerated:** Pt-Sn-MG-AL-DC-2 ~ Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-1 > Pt-Sn-MG-AL-DC-1

Selectivity:

- **Fresh:** Pt-Sn-MG-AL-DC-2 > Pt-Sn-MG-AL-DC-1 > Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-1
- **Regenerated:** Pt-Sn-MG-AL-DC-2 > Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-1 > Pt-Sn-MG-AL-DC-1

Propylene yield:

- **Fresh:** Pt-Sn-MG-AL-DC-2 ~ Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-1 > Pt-Sn-MG-AL-DC-1
- **Regenerated:** Pt-Sn-MG-AL-DC-2 > Pt-Sn-MG-AL-2 > Pt-Sn-MG-AL-1 > Pt-Sn-MG-AL-DC-1

V. CONCLUSION

The Pt-Sn-MG-AL-DC-2 catalyst shows substantially higher propane conversion and maintaining high propene selectivity. Chlorine elimination had evident impacts on the

multiple characteristics of the catalysts, such as acidity, specific surface area, pore volume, etc. The removal of chlorine from the catalysts has an impact on the propylene selectivity. The propane conversion was better for the catalyst with Mg/Al ratio of five mol/mol specifically for Pt-Sn-MG-AL-1 catalyst. However, the propylene selectivity and yield are observed to be better for the Pt-Sn-MG-AL-DC-2 catalyst. It is observed that the effect of both Mg/Al ratio and dechlorination has considerable impact on the catalyst characteristics.

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REFERENCES

- [1] N.A. Pakhomov, V.N. Kashkin, E.I. Nemykina, V.V. Molchanov, V.I. Nadochiy, A.S. Noskov, "Dehydrogenation of C3-C4 paraffins on Cr2O3/Al2O3 catalysts in fluidized and fixed bed reactors", Chem. Eng. J., vol. 154, pp.185-188, 2009.
- [2] M.A. Chen, J. Xu, Y. Cao, H.Y. He, K.N. Fan, J.H. Zhuang, "Dehydrogenation of propane over In2O3-Al2O3 mixed oxide in the presence of carbon dioxide", J. Catal., vol. 272, pp.101-108, 2010.
- [3] S. Pisduangdaw, J. Panpranot, C. Methastidsook, C. Chaisuk, K. Faungnawakij, P. Praserttham, O. Mekasuwandumrong, "Characteristics and catalytic properties of Pt-Sn/Al2O3 nanoparticles synthesized by one-step flame spray pyrolysis in the dehydrogenation of propane", Appl. Catal. A: Gen., vol. 370, pp. 1-6, 2009.
- [4] B. S.A. Bocanegra, A.A. Castro, O.A. Scelza, S.R. de Miguel, "Characterization and catalytic behavior in the n-butane dehydrogenation of trimetallic InPtSn/MgAl2O4 catalysts", Appl. Catal. A: Gen., vol.333, pp.49-56, 2007.
- [5] S.A. Bocanegra, A. Guerrero-Ruiz, S.R. de Miguel, O.A. Scelza, "Performance of PtSn catalysts supported on MAI2O4 (M: Mg or Zn) in n-butane dehydrogenation: characterization of the metallic phase", Appl. Catal. A: Gen., vol.277, pp.11-22, 2004.
- [6] R.D. Cortright, J.M. Hill, J.A. Dumesic, "Selective dehydrogenation of isobutane over supported Pt/Sn catalysts", Catal. Today, vol.55, pp.213-223, 2000.
- [7] M. Tasbihi, F. Feyzi, M.A. Amlashi, A.Z. Abdullah, A.R. Mohamed, "Effect of the addition of potassium and lithium in Pt-Sn/Al2O3

- catalysts for the dehydrogenation of isobutene", *Fuel Proc. Tech.*, vol.88, pp. 883–889, 2007.
- [8] Y. Zhang, Y. Zhou, A. Qiu, Y. Wang, Y. Xu, P. Wu, "Propane dehydrogenation on PtSn/ZSM-5 catalyst: Effect of tin as a promoter", *Catal. Comm.*, vol.7, pp. 860–866, 2006.
- [9] T. Waku, J.A. Biscardi, E. Iglesia, "Catalytic dehydrogenation of alkanes on Pt/Na-(Fe)ZSM5 and staged O₂ introduction for selective H₂ removal", *J. Catal.*, vol. 222, pp.481–492, 2004.
- [10] S.R. Vatcha, F. Trifiro, F. Cavani, in: D. Helius (Ed.), *Oxidative Dehydrogenation and Alternative Dehydrogenation Processes*, Catalytic study number 4992, OD, CA, USA, 1993.
- [11] R.J. Rennard, J. Freil, "The role of sulfur in deactivation for propane dehydrogenation", *J. Catal.*, vol. 98, pp- 235, 1986.
- [12] G. Aguilar-Ríos, M.A. Valenzuela, H. Armendáriz, P. Salas, J.M. Dominguez, D. Acosta, I. Schifter, "Influence of vanadium on the physicochemical and catalytic properties of USHY zeolite and FCC catalyst", *Appl. Catal. A*, Vol. 90, pp. 35, 1992.
- [13] G. Aguilar-Ríos, M.A. Valenzuela, P. Salas, H. Armendáriz, P. Bosch, G. Del Toro, R. Silva, V. Bert'in, S. Castillo, A. Ramirez-Solis, I. Schifter, "Hydrogen interactions and catalytic properties of platinum-tin supported on zinc aluminate", *Appl. Catal.*, vol. 127, pp.65, 1995.
- [14] D. Roth, P. Gelin, M. Primet, E. Tena, "Catalytic behaviour of Cl-free and Cl-containing Pd/Al₂O₃ catalysts in the total oxidation of methane at low temperature", *Appl. Catal. A. Gen.*, vol. 203, pp.37-45, 2003.
- [15] S. S. Peri, C. R. F. Lund, "The Role of Chlorine in Induction Periods During the Oxidation of Methane over Pd/SiO₂", *J. Catal.*, vol.152, pp.410-414, 1995..
- [16] E. Marceau, M. Che, J. Saint-Just, J. M. Tatibou, "Influence of chlorine ions in Pt/Al₂O₃ catalysts for methane total oxidation", *Catal. Today*, vol. 29, pp.415-419, 1996.
- [17] N. W. Cant, D. E. Angove, M. J. Patterson, "In situ FT-IR study of NH₃ formation during the reduction of NO_x with propane on H/Cu-ZSM-5 in excess oxygen", *Catal. Today*, vol. 44, pp.93-140, 1998.
- [18] Application Report (Elementar Analyse system GmbH Germany) – Detection of chlorine in combination with traditional elemental analysis (AB-S-261012-E-01).
- [19] M. Paulis, H. Peyrard, M. Montes, "Influence of Chlorine on the Activity and Stability of Pt/Al₂O₃ Catalysts in the Complete Oxidation of Toluene", *J. Catal.*, vol.199, pp.30-40, 2001.
- [20] G. J. Arteaga, J. A. Anderson, C. H. Rochester, "Effects of Catalyst Regeneration with and without Chlorine on Heptane Reforming Reactions over Pt/Al₂O₃ and Pt-Sn/Al₂O₃", *J. Catal.*, vol. 187, pp.219-229, 1999.
- [21] J. Salmones, J.A. Galicia, O. Mart'inez, M.A. Valenzuela and G.Aguilar-R'ios, "Propane dehydrogenation activity of Pt and Pt-Sn catalysts supported on magnesium aluminate: influence of steam and hydrogen", n: *Acta XVI Simp. Iberoam. Catal.*, vol. 1, pp. 277-282, 1998.
- [22] E.J.W. Verwey, E.L. Heilmann, "Physical Properties and Cation Arrangement of Oxides with Spinel Structures I. Cation Arrangement in Spinel", *J. Chem. Phys.*, vol. 15, pp.174, 1947.
- [23] Y.-L. Shan, Yu-Ling Shan, Ting Wang, Zhi-Jun Sui, Yi-An Zhu, Xing-Gui Zhou, "Hierarchical MgAl₂O₄ supported Pt-Sn as a highly thermostable catalyst for propane dehydrogenation", *Catal. Comm.* vol. 84, pp.85–88, 2016.
- [24] B. Li, Z. Xu, F. Jing, S.Luo, Wei Chu, Facile one-pot synthesized ordered mesoporous Mg-SBA-15 supported PtSn catalysts for propane dehydrogenation, *Appl. Catal. A: Gen.* vol. 533, pp.17-27, 2017.
- [25] C. Dai, Y. Li, C. Ning, W.Zhang, X. Wang, C. Zhang, The influence of alumina phases on the performance of Pd/Al₂O₃ catalyst in selective hydrogenation of benzonitrile to benzylamine, *Appl. Catal. A, Gen.* vol. 545, pp.97–103, 2017.
- [26] Z. Yiwei, Z.Yuming, S. Junjun, "Comparative study of bimetallic Pt-Sn catalysts supported on different supports for propane dehydrogenation", 2014.
- [27] Yu Shi, X.Li, Xin Rong, Bin Gu, H. Wei and C. Sun, Influence of support on the catalytic properties of Pt-Sn-K/q-Al₂O₃ for propane dehydrogenation, *RSC Adv.*, vol. 7, pp. 1, 2017.
- [28] S. Won Choi, W.G. Kim, J.S. So, J.S. Moore, Y. Liu, R.S. Dixit, J.G. Pendergast, C. Sievers, D.S. Sholl, S. Nair, and C. W. Jones, "Propane dehydrogenation catalyzed by gallosilicate MFI zeolites with perturbed acidity", *J.Catal.*, vol. 345, pp.113–123, 2017.
- [29] T. Gjervan, R. Prestvik, B. Tøtdal, C. E. Lyman, A. Holmen. "The influence of the chlorine content on the bimetallic particle formation in Pt-Re/Al₂O₃ studied by STEM/EDX, TPR, H₂ chemisorption and model reaction studies", *Catal. Today*, vol. 65, pp.163-169, 2001.
- [30] W.M.H. Sachtler, "Selectivity and rate of activity decline of bimetallic catalysts", *J.Mol.Catal.*, vol. 25, pp. 1-12, 1984.
- [31] M. Sheintucha, O. Lirona, A. Riccab, V. Palma, "Propane dehydrogenation kinetics on supported Pt catalyst", *Appl. Catal. A: Gen.*, vol. 516, pp.17–29, 2016.
- [32] W.Z. Li, L. Kovarik, D. Mei, et al., "Stable platinum nanoparticles on specific MgAl₂O₄ spinel facets at high temperatures in oxidizing atmospheres", *Nat. Comm.*, vol. 4, pp.2481, 2013.
- [33] Y.L. Shan, Y.A. Zhu, Z.J. Sui, et al., "Insights into the effects of steam on propane dehydrogenation over a Pt/Al₂O₃ catalyst", *Catal. Sci. Technol.*, vol. 5, pp.399-4000, 2015.
- [34] M. Fattahi, F. Khorasheh, S. Sahebdehfar, F.T. Zangeneh, K. Ganji, M. Saeedizad, "The effect of oxygenate additives on the performance of Pt-Sn/γ - Al₂O₃ catalyst in the propane dehydrogenation process", *Scientia Iranica*, Vol.18, pp.1377– 1383, 2011.
- [35] H. Armend'ariz A. Guzmán, J.A.Toledo, M.E Llanos, AVázquez, G Aguilar-Ríos., "Isopentane dehydrogenation on Pt-Sn catalysts supported on Al-Mg-O mixed oxides: effect of Al/Mg atomic ratio", *App. Catal A: Gen.*, vol. 211, vol.69–80, 2001.
- [36] Stepanova, L.N., Belskaya, O.B., Leont'eva, N.N., and Likhobolov, V.A., Use of Platinum Carbonyl Complexes in the Synthesis of Pt/MgAlOx Catalysts, *Kin. Catal.*, vol.54, pp.505-510, 2013.
- [37] Belskaya, O.B., Gulyaeva, T.I., Talsi, V.P., Kazakov, M.O.,Nizovskii, A.I., Kalinkin, A.V., Bukhtiyarov, V.I., and Likhobolov, V.A., "Formation of platinum sites on layered double hydroxide type basic supports: III. Effect of the mechanism of (PtCl₆)²⁻ complex binding to aluminum-magnesium layered double hydroxides on the properties of supported platinum in Pt/MgAlO_x catalysts" *Kinet. Catal.*, vol. 55, pp. 786. 2014.
- [38] Mironenko, R.M., Belskaya, O.B., Talsi, V.P., Gulyaeva, T.I., Kazakov, M.O., Nizovskii, A.I.,Kalinkin, A.V., Bukhtiyarov, V.I., Lavrenov, A.V., and Likhobolov, V.A., "Effect of γ-Al₂O₃ hydrothermal treatment on the formation and properties of platinum sites in Pt/γ-Al₂O₃ catalysts", *Appl. Catal., A*, vol. 469, pp. 472, 2014.