# Effect of Addition of Different Promoters on the Performance of Pt-Sn-K/Al$_2$O$_3$ Catalyst in the Propane Dehydrogenation

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**Abstract**

*The effect of the addition of different promoters, namely, La, Ir, Re and Cs to trimetallic Pt-Sn-K/Al$_2$O$_3$ catalyst on its performance in propane dehydrogenation was studied. The reference trimetallic Pt/Sn/K and tetrametallic catalysts Pt/La/Sn/K, Pt/Ir/Sn/K, Pt/Re/Sn/K and Pt/Sn/Cs/K were prepared by sequential impregnation of γ-alumina support. The catalysts were characterized by TPD and TPR tests. Catalytic performance tests were carried out in a fixed-bed quartz reactor for propane dehydrogenation activity and propylene selectivity under representative industrial conditions. The Pt/Sn/Cs/K catalyst showed better performances in terms of propylene yield. The performance of Pt/Sn/Cs/K catalysts was further improved by adjusting its Cs loading. The addition of Cs to Pt-Sn-K/Al$_2$O$_3$ catalyst could improve catalytic performance chiefly through modifying the nature of acidic function of the support.*

**Keywords:** *Propane Dehydrogenation, Pt-Sn Catalysts, Promoter, Catalyst Performance*

## 1- Introduction

Supported platinum-based catalysts are widely used in chemical industries. Platinum is an effective catalyst in the dehydrogenation of alkanes when dispersed on high-surface area supports such as transition alumina. However, the selectivity is poor due to side reactions such as hydrogenolysis and cracking. It can be enhanced by the addition of different promoters to the Pt/Al$_2$O$_3$ catalyst. The influence of promoters on catalyst performance has been extensively studied for formulation of selective catalysts for dehydrogenation of low and high molecular weight paraffins [1]. Typically, one (or more) electronic or geometric modifiers, most commonly Sn, are incorporated in the formulation as promoters. Tin, for instance, neutralizes the acidity of supports, interacts electronically with Pt, and reduces the "ensemble" effect that favors coke formation [2-7].

Alkaline or alkaline earth metals are also commonly used to control the acidity of the support to avoid side reactions on acid sites.

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Interestingly, the basicity of alkali cation appears to effect platinum activity as well [8]. The additional effects might be modifying the active metal dispersion, promoting hydrogen spillover, diminishing the amount of coke formed (not only on the supports, but also on the active metal sites) and increasing the fraction of bare metallic Pt surface after carbon deposition [9-10]. However, an excess of loading of the alkali promoter could destroy the balance of metal function and acid properties, weakening the interaction of Pt and Sn, and thus the catalytic performance decreases [11]. Therefore, an optimum of alkali metals level should exist.

In this work, the effect of the addition of La, Re, Ir and Cs, as additional promoters to the conventional trimetallic Pt-Sn-K/Al₂O₃ catalyst in dehydrogenation of propane is studied. Different ions should exhibit different promoting effects due to their characteristic electronic structure. As Cs showed better promoting effects, the influence of loading the Cs to Pt-Sn-K/Al₂O₃ catalysts on its performance in propane dehydrogenation reaction was investigated.

## 2- Experimental
### 2.1- Catalysts preparation
The catalyst samples were synthesized by successive impregnation of the precursors. A commercial $\gamma$-Al₂O₃ pellet, 1.6 mm in diameter, the textural properties of which are given in Table 1 was used as the support. The support was impregnated with an aqueous solution of $H_2PtCl_6$, acidic solution of $SnCl_2$, $KNO_3$, $IrCl_3$, $Re_2O_7$, $La(NO_3)_3 \cdot 6H_2O$ and $CsNO_3$ to obtain the desired loading (0.7% for Sn; 0.5% for Pt, Ir, Re, La and 0.32% for

K and Cs) of the metal. The sample was dried at 120°C for 12 h. Calcinations were carried out in 550°C for 3 h. Further, four catalyst samples containing Pt (0.5 wt%), Sn (0.7 wt%), K /Al₂O₃ and different loadings of Cs (0.02, 0.04, 0.14, 0.32 wt%), with corresponding potassium loadings such that 0.64% total alkali metal loading was achieved, were synthesized by incipient wetness impregnation of the trimetallic catalyst with $CsNO_3$ solution.

**Table 1.** Summary of textural properties of the support [12].

| Parameter | value |
|---|---|
| Surface area (m²/g) | 196 |
| Average pore diameter (nm) | 10.6 |
| Total pore volume (m³/g) | 0.5 |

### 2.2- Characterization tests
The acidity of the catalysts was characterized by temperature programmed desorption (TPD) of ammonia using Micromeritics 2900. Temperature programmed reduction (TPR) tests were conducted with CHEM BET 3000.

### 2.3- Catalytic runs
Catalytic performance tests for dehydrogenation of propane were carried out in a fixed-bed quartz reactor (ID=15 mm) using a mixture of propane and hydrogen as the feed. Catalyst particles (1.5 g) diluted with 3 g quartz powder (grain size about 1 mm) was packed in the reactor. The catalyst was reduced in hydrogen flow at 530 ºC for 1 h in the reactor. The test conditions were selected close to industrial operating conditions, that is, the weight hourly space velocity (WHSV), temperature (*T*) and

H₂/CH were 1.7 h$^{-1}$; 615°C and 0.87 mol/mol, respectively; and the operating pressure was 0.87 atm. The reactor effluent was analyzed for light hydrocarbons by an online gas chromatograph (Agilent 6890N), equipped with TCD and FID detectors. Propane ($C_3$) conversion and selectivity to the respective products were calculated as [13]:

Propane conversion (mol %)
=(moles of $C_3$ reacted/moles of $C_3$ fed) $\times 100$

Selectivity to species i (mol%)=
(moles of product i formed/ moles of $C_3$ reacted)
$\times(N_i/N_{C3})\times$ 100

where *i* stands for propylene, ethylene, ethane and methane; and $N_i$ and $N_{C3}$ are number of carbon atoms per molecule in the product and propane, respectively.

## 3- Results and discussion
### 3.1- Characterization results
Figure 1 shows the TPR profile for the Pt-Sn-K/Al₂O₃ reference catalyst. Three reduction peaks are observed at 293, 695 and 843 °C. The first one is related to reduction of Pt species (that is, platinum oxide species and/or oxychlorplatinum surface complex, [PtO$_x$Cl$_y$] $_s$ [14]). The second peak is related to the reduction of the Sn species that can be reduced easily, which interacts strongly with Pt, while the third peak around is assigned to the reduction of the tin species that interacts strongly with the support [15]. In fact, when alumina is used as the support; the reduction of Sn to the metallic state is very difficult [16], probably because it is stabilized by the support forming tin aluminates species [17].

A comparison of the reduction peaks related to Sn from TPR results shows the La shifts the reduction peak of Sn to lower temperatures (Table 2). This effect could be due to the interaction between the Sn and La atoms. Atoms with 4*f* orbital exhibit poor shielding properties, thereby, the $Z_{eff}$ (nuclear charge) increases and results in more compact atoms. Reduction of Sn is essential for its interaction and promoting effect with platinum to reduce the "ensemble effect" that favors coke formation and other side-reactions.

**Table 2.** Results of TPR tests

| Sample | Reduction peak related to Sn (°C) |
|---|---|
| Pt/Sn/Re/K | 580 |
| Pt/Sn/Ir/K | 537 |
| Pt/Sn/La/K | 433 |
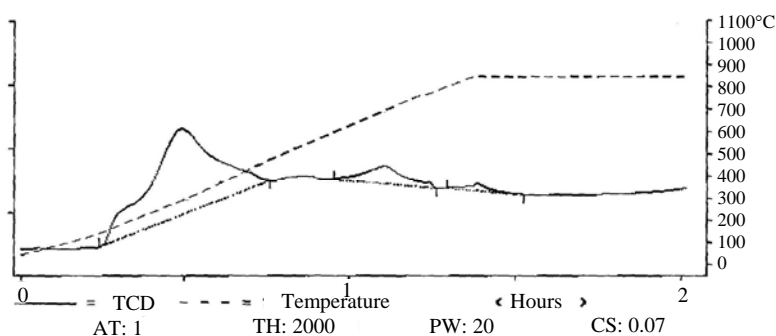


**Figure 1.** TPR spectrum for Pt-Sn-K/Al₂O₃ catalyst

The poisoning effect of the alkali metals on the acidic sites of alumina was studied by NH$_3$-TPD test. The addition of Cs, which neutralized both the weak and strong acid sites with the latter, appear to suffer more. Table 3 shows two peaks: a main one at about 350ºC corresponding to weak acid sites and a second one at about 708 ºC corresponding to medium to strong acid sites. For the trimetallic catalyst (Pt-Sn-K/Al$_2$O$_3$), when Cs is added desorption temperature peaks shift to lower temperatures, that is, 345 and 694°C, respectively. Surface acidity of the support is also decreased by adding Cs. The strong acid sites on catalysts are poisoned by the addition of small quantities of alkali metal ions. Further addition of these ions blocks centers with lower acid strength.

**3.2- Catalyst performance**
Plots of catalyst performances in terms of propane conversion, propylene selectivity and propylene yield are illustrated in Figs. 2, 3 and 4, respectively. The four catalysts show close trends and performances during warm-up, and then, steady temperature regime (615ºC) of the reactor. However, Cs-promoted catalyst exhibits slightly better performance in terms of propylene yield. Cesium, as an alkali metal neutralize acid sites of the support, decreasing the ratio of acid sites to active sites and therefore,

imhibit side reactions such as cracking and dehydrocylization, which require acidic sites and are also conductive to coke formation The examination of spent catalysts lacking Cs showed a higher coke deposition which might be due to the higher acidity of the sample.
The effect of La on the performance of Pt-Sn catalysts can be explained by the fact that Pt and Sn are less tightly bound together than they are in the cluster compounds. La atoms can easily squeeze in between the Pt and Sn atoms which can decrease the reduction of Sn resulting from the spillover of H$_2$ on Pt. It can also prevent the excessive formation of metallic Sn in the Pt-Sn alloy, which is detrimental to the catalytic activity. In Pt-Sn metal cluster catalysts La cannot squeeze between the Pt and Sn since they are chemically bonded. Consequently, La can only inhibit the coagulation of the catalytic active centers during reduction, and can hardly minimize the excessive reduction of Sn from the spillover of hydrogen on Pt [18]. Therefore, the effect of anti-reduction is more prominent in conventional La-containing catalysts and the effect of La on the conventional catalysts is much larger than on the metal cluster catalysts. It has been found that the increasing amount of La added had no obvious effect on the activity and selectivity of Pt-Sn catalyst [19].

**Table 3.** Results of NH$_3$-TPD test

| Catalyst sample | Desorption temperature related to first peak (°C) | Desorption temperature related to second peak (°C) | Surface acidity ($10^{-3}\times$-mol/g) |
|---|---|---|---|
| Pt(0.5)Sn(0.7)K(0.32) | 350 | 708 | 10.86 |
| Pt(0.5)Sn(0.7)K(0.32)Cs(0.32) | 345 | 694 | 9.74 |
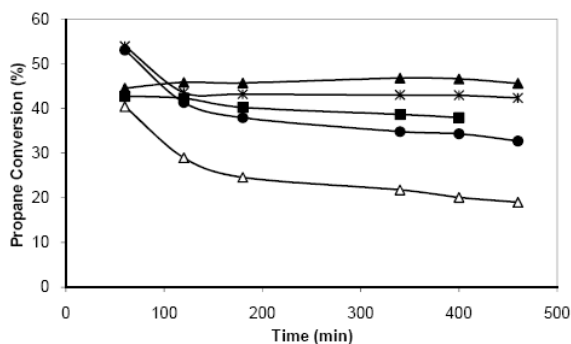
**Figure 2.** Comparison of propane conversion for (●) Pt/Sn/K/La, (■) Pt/Sn/K/Ir, (▲) Pt/Sn//K/Cs, (Δ) Pt/Sn/K/Re and (*) Pt/Sn/K on γ- alumina supports (WHSV=1.7 h$^{-1}$; $T$=615°C; H$_2$/CH: 0.87).
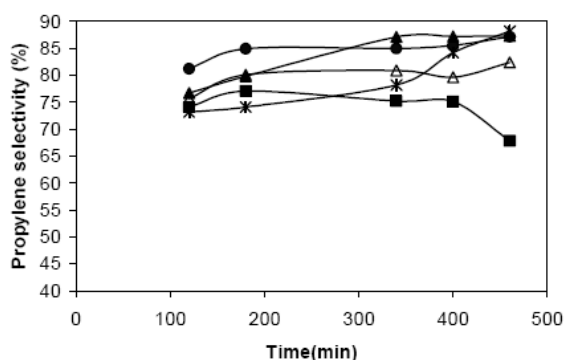


**Figure 3.** Comparison of propylene selectivity for (●) Pt/Sn/K/La, (■) Pt/Sn/K/Ir, (▲) Pt/Sn//K/Cs, (Δ) Pt/Sn/K/Re and (*) Pt/Sn/K on γ- alumina supports (WHSV=1.7 h$^{-1}$; $T$=615°C; H$_2$/CH: 0.87).
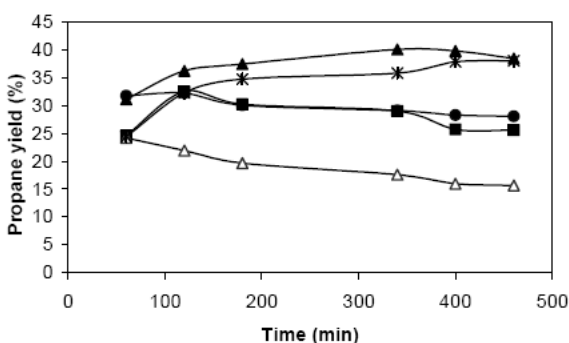


**Figure 4.** Comparison of propylene yield for (●) Pt/Sn/K/La, (■) Pt/Sn/K/Ir, (▲) Pt/Sn//K/Cs, (Δ) Pt/Sn/K/Re and (*) Pt/Sn/K on γ- alumina supports (WHSV=1.7 h$^{-1}$; $T$=615°C; H$_2$/CH: 0.87).

Figures 5, 6 and 7 illustrate the influence of Cs loading variation, while maintaining total alkaline metal loading at 0.64% on propane conversion propylene selectivity and propylene yield, respectively. A comparable performance is observed in the lower concentration of Cs. The PtSnK$_{0.32}$Cs$_{0.32}$ catalyst exhibits the highest activity. Cesium could electronically modify the metallic active phase as well. Cs binds to Pt in two ways: donation of electron density to a metal orbital of δ symmetry and back-donation of metal electron density from a metal orbital in to orbital of same symmetry, i.e., the empty $\pi^*$ orbital of Cs. As the entering group in a substitution reaction approaches, the electron density of the metal is increased and any metal orbital that can remove the excess density should stabilize the transition state.
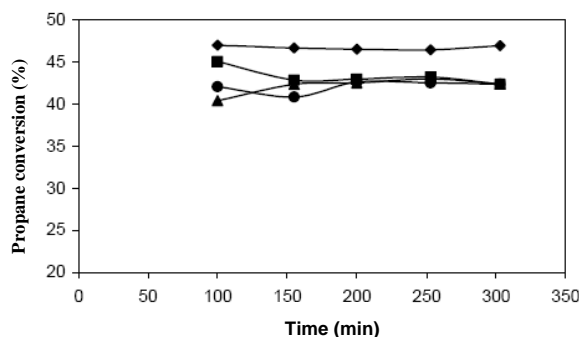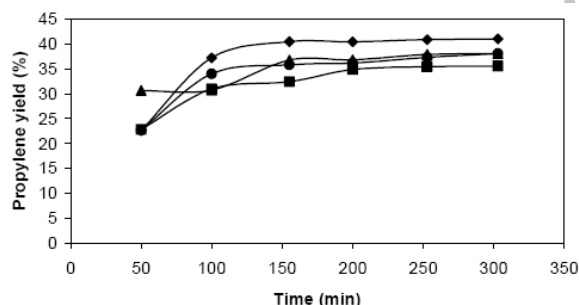


**Figure 5.** Comparison of propane conversion between different Cs concentration on (♦) PtSnK$_{0.32}$Cs$_{0.32}$, (■) PtSnK$_{0.5}$Cs$_{0.14}$, (▲) PtSnK$_{0.6}$Cs$_{0..04}$, and (●) PtSnK$_{0.62}$Cs$_{0..02}$ (WHSV=1.7 h$^{-1}$; $T$=615°C; H$_2$/CH: 0.87).

In this work the total loading of alkaline metal was maintained constant to obtain a more resolved understanding on the effect of alkaline metal type, that is, to decouple the overall promoting effect from the neutralizing effect. Otherwise, excessive

addition of alkaline metal increases the weak Lewis acid sites and promote the tin species to be reduced to metallic tin. In this instance, the cracking and hydrogenolysis of propane could be carried out easily, which was disadvantageous to the dehydrogenation [10].
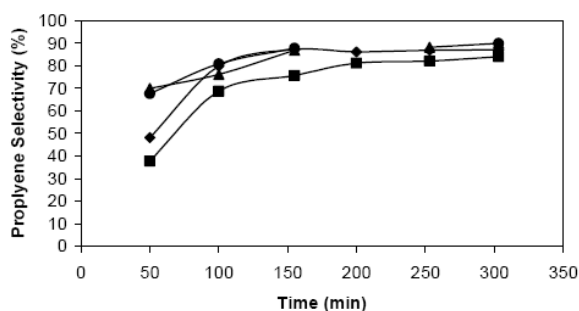


**Figure 6.** Comparison of propylene selectivity between different Cs concentration on (♦) $PtSnK_{0.32}Cs_{0.32}$, (■) $PtSnK_{0.5}Cs_{0.14}$, (▲) $PtSnK_{0.6}Cs_{0..04}$, and (●) $PtSnK_{0.62}Cs_{0..02}$ (WHSV=1.7 h$^{-1}$; $T$=615$^{\circ}$C; H₂/CH: 0.87).



**Figure 7.** Comparison of propylene yield between different Cs concentration on (♦) $PtSnK_{0.32}Cs_{0.32}$, (■) $PtSnK_{0.5}Cs_{0.14}$, (▲) $PtSnK_{0.6}Cs_{0.04}$, and (●) $PtSnK_{0.62}Cs_{0..02}$ (WHSV=1.7 h$^{-1}$; $T$=615$^{\circ}$C; H₂/CH: 0.87).

## 4- Conclusions

Comparison of La, Ir, Re and Cs as promoters shows that Cs exhibit superior promoting effects on trimetallic γ-alumina supported platinum catalyst in dehydrogenation of propane. This effect could be attributed to modifying the nature of acidic function and the metallic phase (by geometric modification of the metallic phase). Among the catalyst samples synthesized, $PtSnK_{0.32}Cs_{0.32}$ sample exhibits the highest propane dehydrogenation performance. The promoting effect of the alkali metals on catalyst performance and the acid character of the alumina support increases with the ionic radius.

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