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# Propane oxidation and steam reforming over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst: effects of the reactant composition and steam

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**Abstract:** The effects of reactant composition and steam on propane combustion over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst were investigated. Propane conversion and the oxidation state of palladium were strongly affected by the redox ratio of reactants. Higher propane conversion could be obtained under rich conditions and explained as a complex balance between oxidation and steam reforming. Water produced in the oxidation could promote the propane conversion by steam reforming. However, the presence of excess steam would bring about inhibition.

**Keywords:** propane; palladium; perovskite; redox ratio; steam

## Introduction

Recently, the oxidation of propane over supported noble metal catalysts has been investigated extensively (Yazawa, 1998; 1999; Noronha, 2000; Maillet, 1997). However, few of these studies have involved the use of stoichiometric or propane-rich mixtures. Such studies are important because these conditions are likely to be encountered in the auto-exhaust gases, especially when the vehicle is first started (a cold-start) (Lafyatis, 1998; Kirchner, 1997).

Palladium is the active component in catalytic conversion of some hydrocarbons. It has been widely accepted that the catalytic activity changes with the oxidation state of palladium, which will depend on factors such as the preparation method, the support (Ciuparu, 2001; Euzen, 1999; Widjaja, 1999), the hydrocarbon (Ferhat-Hamida, 2001), the stoichiometry of the reaction mixture (Yazawa, 1998; Deng, 1999), and the time of exposure to a particular reaction mixture (Burch, 1999). Steam, presented in the exhaust, also has important effects on the performance of palladium catalyst (Barbier, 1994; Maillet, 1996).

Most of these Pd catalysts are supported on simple metal oxides, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> (Ozkan, 1998; Shen, 2001). It is well known that perovskite-type oxides have good thermal stability and considerable oxidation activity for hydrocarbon. However, using perovskite-type oxides as support materials was relatively seldom.

The present work is concerned with oxidation activity for propane over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst. The effects of the redox ratio of reactants and the presence of steam on the catalytic activity are investigated in detail. Our aim is to aid the development of Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst for propane abatement.

## 1 Experimental

### 1.1 Catalysts preparation

LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> was prepared by using a conventional coprecipitation method. In the synthesis process, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>HCO<sub>3</sub>·H<sub>2</sub>NCOONH<sub>4</sub> (all in AR grade purity) were used. A solution of the metal nitrates of appropriate La, Fe and Co concentrations was prepared and then added to a solution of ammonium carbonate. The precipitate was washed, dried at 120°C for 24 h, calcined in air at 900°C for 10 h, and then the powdered LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> was obtained. 2 wt. % Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> was prepared by impregnating a LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> carrier with an aqueous solution containing a desired amount of PdCl<sub>2</sub> (AR grade). After drying at 120°C, the catalyst was calcined at 600°C for 5 h in air. All catalyst samples were pressed and sieved to a size of 20—40 meshes for the activity evaluation.

### 1.2 Catalytic activity evaluation

The activity measurements were carried out in a fixed-bed quartz tubular reactor at atmospheric pressure. Catalyst particles (4 ml) were placed in the reactor. Inlet temperature was measured at the place of 2 mm from the front side of the catalyst bed. The temperature inside the reactor was increased continuously from 150°C to 500°C at a rate of 5°C·min<sup>-1</sup>, while the reactant gases went through the reactor with a space velocity of 50000 h<sup>-1</sup>.

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Table 1 gives the inlet gas concentrations of the reactants employed for the different reactions investigated in this study: propane oxidation with and without steam, and propane steam reforming reactions. The concentration of propane in the reaction mixture was 0.2% and that of oxygen was changed from 0.74% to 1.9%. Inlet concentration of H<sub>2</sub>O was maintained at 10% in the case of a “wet” gas mixture. Nitrogen was used as a balance gas. The S value represents the redox ratio of the reactants, defined as:  $S = [O_2]/5[C_3H_8]$ . When S is < 1.0, 1.0, and > 1.0, the composition of the feed stream is rich, stoichiometric and lean, respectively.

The products were analyzed by gas chromatography (Maillet, 1996) and an AVL DiGas 4000 was used as an aided detector.

### 1.3 Catalysts characterization

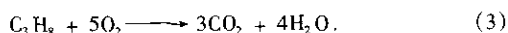
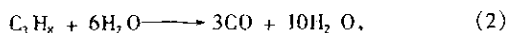
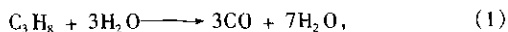
BET-surface area of catalysts was measured by N<sub>2</sub> adsorption using the single point method. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-RB diffractometer with Cu K $\alpha$  radiation. XPS allowed us to follow the oxidation state of palladium during the propane oxidation in dry mixture. After interruption of the reaction at certain temperatures, the catalyst was quickly cooled down to room temperature under nitrogen and subjected to XPS analysis. XPS measurements were conducted on a VG ESCA LAB 220 i-XL system with Al K $\alpha$  radiation under UHV ( $5 \times 10^{-9}$  Pa), calibrated internally by carbon deposit C (1s) binding energy (BE) at 284.6 eV.

**Table 1** Gas compositions for activity test (nitrogen was used as a balance gas)

Reaction	Gas composition, vol. , %		
	C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	H <sub>2</sub> O
Oxidation without steam	0.5	0.74 to 1.9	–
Oxidation in presence of steam	0.5	0.74 to 1.9	10
Steam reforming	0.5	–	10

1.9). It can be seen that the perovskite-only catalyst has good propane oxidation activities. The temperature for 50% conversion in the propane oxidation was about 400°C over the LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst regardless of the reactant gas composition. The enhancement of the oxidation activity by palladium loading is evident. The temperature for 50% conversion was lowered to about 320°C with palladium loading of 2% (wt. %). It can be concluded that both perovskite and palladium are active for propane oxidation and the palladium sites are the primary centers of the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst.

The redox ratio(S) of the reactant composition also plays an important role in the propane oxidation. Over the LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst, the temperature for 50% conversion in the propane combustion was 390°C and 413°C in rich ( $S = 0.85$ ) and lean ( $S = 1.9$ ) gas compositions, respectively. The reason the activity in lean condition is relative poorer is unknown. It is possible because that the active sites are blocked by excess adsorbed oxygen. In the case of the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst, the reactant composition has no influence on the activity at temperatures below 325°C. However, the propane conversion with  $S = 0.85$  was much higher than that with  $S = 1.9$  at temperatures above 345°C. Product analysis showed that propane steam reforming (Eqs. 1 and 2) occurred when oxygen was totally consumed in the former case (H<sub>2</sub>O needed in steam reforming came from propane oxidation (Eq.3)).



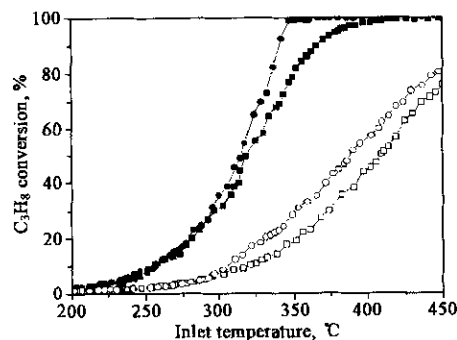
To reveal the reaction mechanism over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst at higher conversions (above 30%), the propane combustion activity was investigated in detail. The propane conversion as a function of the

## 2 Results

### 2.1 Catalytic activity

#### 2.1.1 Propane oxidation over LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> and Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub>

Fig. 1 shows the curves “conversion %” vs. “inlet temperature”, obtained on LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> and Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalysts by varying the redox ratio S (0.85 or



**Fig. 1** Temperature-programmed oxidation of propane without steam at 5°C · min<sup>-1</sup> over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst in the mixture of  $S = 1.9$  (■) and 0.85 (●) and LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst in the mixture of  $S = 1.9$  (□) and 0.85 (○).

$S$  value is depicted in Fig. 2. The propane conversion increased with the increase in the  $S$  value below 340°C. However, the propane conversion appreciably changed above 345°C with the reaction atmosphere ( $S$  value). It was steeply increased with the slightly decrease in the  $S$  value when  $S < 1$ , though it still increased with the increase in the  $S$  value under lean conditions, and the minimum conversion was obtained in the neighborhood of stoichiometric atmosphere ( $S = 1$ ).

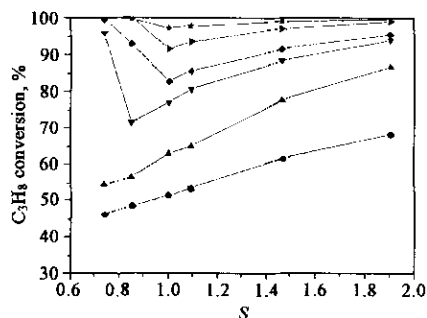


Fig.2 Oxidation of propane without steam over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst at different constant temperatures: 325°C (●), 335°C (▲), 340°C (▼), 345°C (◆), 360°C (▸) and 390°C (★) effect of the  $S$  value

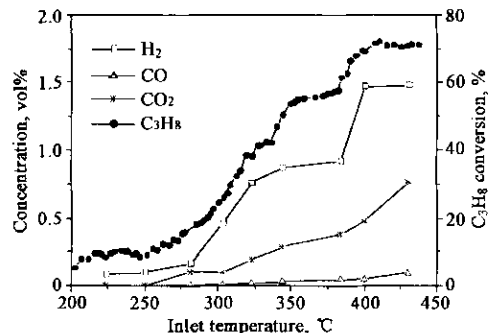


Fig.3 Temperature-programmed steam reforming of propane at 5°C min<sup>-1</sup> over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst: propane conversion and concentrations of products as functions of inlet temperature

### 2.1.2 Product distribution in propane steam reforming

Fig. 3 shows the product distribution and propane conversion against the inlet temperature of propane steam reforming (10% H<sub>2</sub>O + 0.5% C<sub>3</sub>H<sub>8</sub>) over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst. The reaction started even at 200°C and the propane conversion increased with the increase of the inlet temperature. The maximum propane conversion, about 70%, was obtained above 400°C. The steam reforming products were formed, namely hydrogen (H<sub>2</sub>), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>).

### 2.1.3 Propane oxidation in presence of steam

Figs. 4 and 5 show the propane oxidation activities in presence of steam (10%) over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst under the mixture of  $S = 1.9$  and 0.85, respectively. For the purpose of comparison, the curves already obtained for  $S = 1.9$  and 0.85 without steam (oxidation) are also reported.

As can be seen from Fig. 4 and 5, the propane conversion was significantly decreased by the presence of steam, especially under rich conditions ( $S = 0.85$ ). The temperature for 50% conversion increased to about 360°C in presence of steam, while it was only 320°C when steam was absent. In addition, oscillatory behavior during propane oxidation over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst was observed in presence of steam and the possible reasons will be discussed next.

The effects of  $S$  value on the propane oxidation in presence of steam are also investigated in detail and the results are shown in Fig. 6. The shapes of the curves are similar to that obtained without steam (Fig. 2) except that the temperatures needed for the same conversions were higher when steam was present in the mixture.

The results of activity tests show that steam has two roles in propane oxidation: little amount of steam (coming from the oxidation in present study) promotes the steam reforming reaction and enhances the propane conversions on one hand, and too much steam seems to deactivate the reaction on the other, especially under rich conditions.

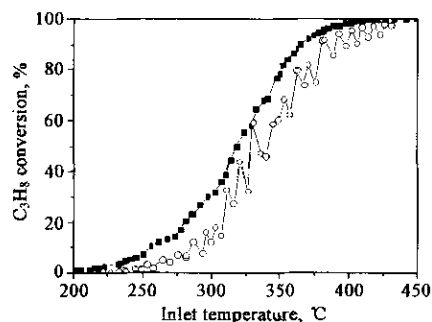


Fig.4 Temperature-programmed oxidation of propane at 5°C min<sup>-1</sup> over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst in the mixture of  $S = 1.9$ . Effect of the presence of steam: no steam (■) (obtained from the results in Fig. 1) and 10% steam (○)

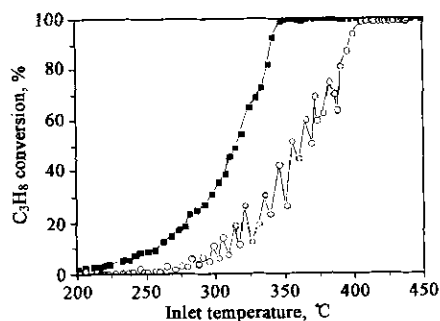


Fig. 5 Temperature-programmed oxidation of propane at  $5^{\circ}\text{C min}^{-1}$  over  $\text{Pd/LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$  catalyst in the mixture of  $S = 0.85$ . Effect of the presence of steam: no steam (■) (obtained from the results in Fig. 1) and 10% steam (○)

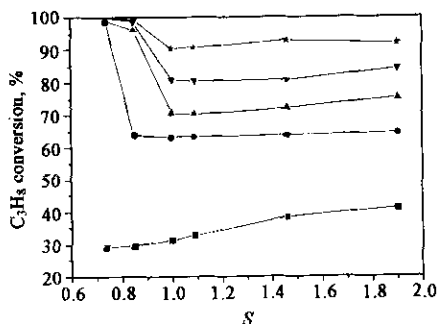


Fig. 6 Oxidation of propane over  $\text{Pd/LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$  catalyst at different constant temperatures:  $350^{\circ}\text{C}$  (■),  $375^{\circ}\text{C}$  (●),  $385^{\circ}\text{C}$  (▲),  $400^{\circ}\text{C}$  (▼) and  $415^{\circ}\text{C}$  (★) effect of the  $S$  value

## 2.2 Characterization of catalysts

### 2.2.1 BET areas and XRD patterns

Conventional coprecipitation methods were employed in the present study as stated above. In order to obtain crystalline perovskites, calcination at high temperatures is necessary, so the areas of the catalysts were relatively small. The BET area of the  $\text{Pd/LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$  catalyst was found to be  $< 7 \text{ m}^2 \cdot \text{g}^{-1}$ .

The crystal compositions of the catalysts were determined by XRD and shown in Fig. 7. The only crystalline structure is identified of  $\text{LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ . Addition to perovskite phase, a small peak at ca.  $33$  ( $2\theta$ -theta value) is assigned to  $\text{PdO}$  (Noh, 1999) over  $\text{Pd/LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ . No additional lines can be found in the XRD patterns.

### 2.2.2 XPS spectra

XPS measurements were carried out on the catalyst after interruption of the propane oxidation run in the mixture of  $S = 1.9$  and  $0.85$ . Two different temperatures were chosen:  $345^{\circ}\text{C}$ , when steam reforming starts in the mixture of  $S = 0.85$ , and  $410^{\circ}\text{C}$ , when the propane conversion reaches 100%. The results are presented in Figs. 8 and 9. The spectrum "before", obtained with the fresh catalyst, is also reported.

Fig. 8(a) shows the  $\text{Pd } 3d_{5/2}$  peak of the fresh sample. The peak appeared at  $336.6 \text{ eV}$ . This kind of palladium can be assigned to oxidized form (Yazawa, 1998; Cubeiro, 1998).

As shown in Fig. 8(b), at  $345^{\circ}\text{C}$ , the  $\text{Pd } 3d_{5/2}$  peak appeared at  $336.6 \text{ eV}$  with shoulder at  $335.0 \text{ eV}$  under the mixture of  $S = 1.9$ . The spectra could be deconvoluted to the two peaks centered at  $336.6$  and  $335.0 \text{ eV}$ , assigned to palladium (II) oxide and metallic palladium, respectively. The fraction of metallic palladium was estimated from the area intensities of the metallic palladium and the palladium oxide and the data are shown in Table 2. The results indicate that most of the palladium was still in the form of  $\text{PdO}$ . However, under the mixture of  $S = 0.85$ , the  $\text{Pd } 3d_{5/2}$  peak appeared at  $335.0 \text{ eV}$  with shoulder at  $336.6 \text{ eV}$  (Fig. 8(c)). The results shown in Table 2 indicate that most of the palladium on the surface was reduced to metallic palladium ( $\text{Pd}^0$ ). Only about 12.8% of the palladium was in the form of  $\text{PdO}$ .

When the propane conversion reaches 100% at  $410^{\circ}\text{C}$ , all the palladium was reduced into  $\text{Pd}^0$  in the mixture of  $S = 0.85$ , and there was still about 17.8% of the palladium in the form of  $\text{PdO}$  in the mixture of  $S = 1.9$ . The spectra are presented in Fig. 9 and the resulting information is collected in Table 3.

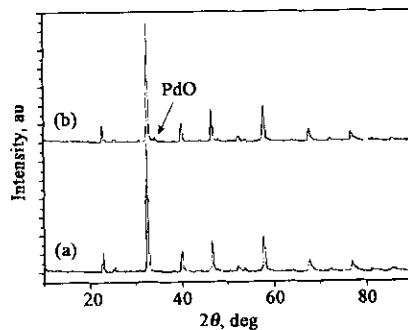


Fig. 7 XRD patterns for: (a)  $\text{LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$  and (b)  $\text{Pd/LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$

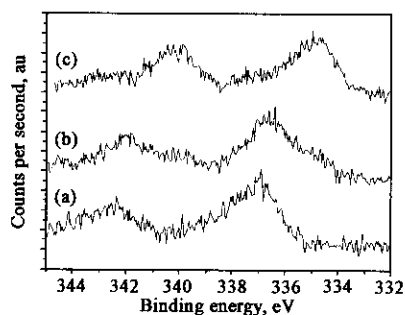


Fig. 8 XPS Pd 3d spectra of the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst before (a) and after interruption of the propane oxidation (without steam) at 345 °C in the mixture of  $S = 1.9$  (b) and 0.85 (c)

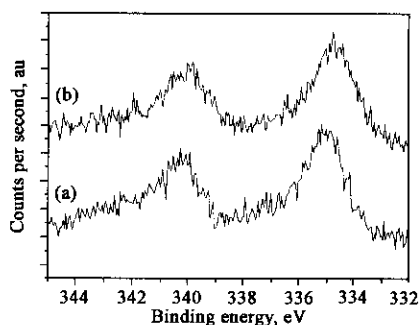


Fig. 9 XPS Pd 3d spectra of the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst after interruption of the propane oxidation (without steam) at 410 °C in the mixture of  $S = 1.9$  (a) and 0.85 (c)

### 3 Discussion

#### 3.1 The effects of the chemical state of palladium on the propane conversion

The propane conversion strongly depended on the  $S$  value as shown in Fig. 2. In addition, in the course of the oxidation reaction, chemical transformations of palladium ( $\text{PdO} > \text{Pd}$ ) can occur. The transformation also depended on the  $S$  value: palladium was more reduced under the rich condition. These results suggest that the propane conversion is affected by the oxidation state of palladium.

Yazawa *et al.* (Yazawa, 1998) reported that the increase in the ratio of oxidized palladium enhanced the propane conversion in the range  $1 < S < 5.5$ . The present results suggest that this is also the case at the temperatures below 340 °C. However, the propane conversion steeply increased from stoichiometric to rich conditions at the temperatures above 345 °C as shown in Fig. 2. The XPS data showed that most of the palladium on the catalyst surface was reduced to metallic palladium ( $\text{Pd}^0$ ) during the catalytic run under rich conditions. In addition,  $\text{H}_2$  and CO could be detected in the exhaust when oxygen was totally consumed, indicating propane steam reforming occurred. These results clearly show that the reduced palladium is more active than partially oxidized palladium in propane steam reforming and gives the highest propane conversion, although the partially oxidized palladium is most active for propane oxidation. Then, the phenomena observed in Fig. 2 above 345 °C could be explained as a complex balance between oxidation and steam reforming. The minimum conversions observed under stoichiometry most probably because steam reforming cannot occur and the rate of oxidation was relatively slower. Higher conversions can be obtained when both oxidation and steam reforming can occur. The results of Maillet *et al.* (Maillet, 1996) indicate that this is also the case with propane combustion over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

Table 3 The fraction of metallic and oxidized palladium on the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst after the propane oxidation (without steam) at 410 °C in the mixture of  $S = 1.9$  and 0.85

Reaction conditions	Fraction of metallic palladium, %	Fraction of oxidized palladium, %
Oxidation without steam ( $S = 1.9$ )	82.2	17.8
Oxidation without steam ( $S = 0.85$ )	100	0

Table 2 The fraction of metallic and oxidized palladium on the Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst before and after interruption of the propane oxidation (without steam) at 340 °C in the mixture of  $S = 1.9$  and 0.85

Reaction conditions	Fraction of metallic palladium, %	Fraction of oxidized palladium, %
Fresh catalyst	0	100
Oxidation without steam ( $S = 1.9$ )	33.5	66.5
Oxidation without steam ( $S = 0.85$ )	87.2	12.8

#### 3.2 The effects of the steam

The activity tests show that the presence of steam in the inlet gases is not necessary for steam reforming to occur: there is sufficient water produced in the oxidation. However, the presence of excess steam depressed the propane conversion, especially under rich conditions. The inhibition under lean conditions is probably due to the formation of inactive  $\text{Pd}(\text{OH})_2$ .

species on the active PdO surface, as suggested by Cullis *et al.* (Cullis, 1972).

Maillet *et al.* (Maillet, 1996) suggested that the presence of steam seemed to maintain the oxidized form of palladium, which is less active than the reduced form for steam reforming as discussed above. Therefore, the depression of the steam reforming may be another reason for the more severe depression under rich conditions.

In addition, oscillatory behavior during propane oxidation over Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst was observed in presence of steam. Numerous reports have appeared in the literature dealing with observed oscillatory behavior in heterogeneous catalytic reaction systems and their interpretation based on different mechanisms and mathematical modeling. Burch *et al.* (Burch, 1999) reported that water also severely inhibits the methane combustion reaction on palladium. An interesting point concerning H<sub>2</sub>O is that the release of H<sub>2</sub>O involves a dehydroxylation of the surface to recreate surface oxide sites (e.g. on PdO), which are required for C-H bond activation. As mentioned above, at a given temperature during propane oxidation in presence of steam, if the rate of dehydroxylation is lower than that of C-H bond activation, then suddenly the rate of propane oxidation drops to a lower value. However, the effect is reversible and therefore not due to permanent deactivation. An oscillatory behavior then develops with increasing temperature, the amplitude and the period of which will depend on the relative rates of dehydroxylation and the kinetics of C-H bond activation from these sites.

## 4 Conclusions

Pd/LaFe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> catalyst was found to be very active in the propane combustion. The activities were strongly affected by the reactant compositions. Propane conversion under rich conditions can be explained as a complex balance between oxidation and steam reforming. Higher conversions can be obtained when both oxidation and steam reforming can occur. However, the presence of excess steam depressed the reaction, especially under rich conditions.

Catalyst characterization by XPS revealed that the reduced palladium was active for the steam reforming, while partially oxidized palladium was the active site of the oxidation.

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