

# Deep oxidation of propane on Pt-supported catalysts: drastic turnover rate enhancement using zeolite supports

T.F. Garetto, E. Rincón, C.R. Apesteguía\*

*Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina*

Received 11 July 2003; received in revised form 2 October 2003; accepted 14 October 2003

## Abstract

The combustion of propane was studied on Pt supported on MgO, alumina, and zeolites KL, HY, ZSM5 and Beta. Samples contained a similar amount of Pt, between 0.32 and 0.44%, and were characterized by employing a variety of physical and spectroscopic techniques. The catalyst activities were evaluated through both conversion versus temperature (light-off curves) and conversion versus time catalytic tests. Kinetic studies showed that the reaction is first order in propane, and zero (Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/MgO) or negative (Pt/zeolites) orders in oxygen. Apparent activation energies ( $E_a$ ) and pre-exponential factors ( $A$ ) were determined and it was verified that the experimental data obey a Constable relation ( $\ln A = mE_a + c$ ). Pt/Al<sub>2</sub>O<sub>3</sub> catalysts of different metallic dispersions were prepared for investigating the effect of Pt crystallite size on combustion activity. It was found that propane oxidation is a structure insensitive reaction on Pt/Al<sub>2</sub>O<sub>3</sub>. Propane oxidation turnover rates (TOF) followed the order: Pt/MgO < Pt/Al<sub>2</sub>O<sub>3</sub> << Pt/KL < Pt/HY ≤ Pt/ZSM5 < Pt/Beta. The TOF values on Pt/acid zeolites were more than two orders of magnitude higher than on Pt/Al<sub>2</sub>O<sub>3</sub>. Propane oxidation activity was also significantly higher on Pt/KL as compared to Pt/Al<sub>2</sub>O<sub>3</sub>, despite that Al<sub>2</sub>O<sub>3</sub> and zeolite KL supports exhibited similar acid sites density and strength. This result showed that the support acid strength did not have a major influence on propane combustion activity. Areal propane uptake was more than one order of magnitude higher on Pt/zeolites than on Pt/Al<sub>2</sub>O<sub>3</sub> and this drastic increase in the density of propane adsorbed species may promote the alkane oxidation rate. It is proposed that the enhanced combustion activity obtained on Pt/zeolites is associated with an additional oxidation pathway from propane adsorbing on the metal-oxide interface region and reacting with oxygen spilled-over from the metal surface.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Propane combustion; Pt catalysts; acid zeolites

## 1. Introduction

Platinum supported on alumina carriers are widely employed for the combustion of non-halogenated volatile organic compounds [1,2]. Particularly, platinum-based catalysts are highly active for oxidative removal of small amounts of hydrocarbon from gaseous or liquid streams. Excepting for palladium in the case of methane, platinum is recognized to be the most active metal for hydrocarbon oxidation [3,4]. However, stable lower alkanes such as propane require relatively high temperatures to be completely oxidized over Pt/Al<sub>2</sub>O<sub>3</sub> and increasing research work has been lately undertaken for developing more active hydrocarbon oxidation catalysts.

Recent papers have reported that the Pt/Al<sub>2</sub>O<sub>3</sub> activity for propane combustion may be substantially increased by alumina sulfation [5–8] or by the addition of electrophilic additives to the support [9,10]. In the case of the promotion of propane oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> by SO<sub>2</sub>, it is believed that the formation of stable sulfate species at the Pt/support interface facilitates the dissociative chemisorption of propane and thereby enhances the intrinsic oxidation activity of platinum [6,7]. The additive effect on the propane combustion on Pt/Al<sub>2</sub>O<sub>3</sub> was investigated by Yasawa et al. [9] by incorporating to the support several additives, such as Na, Cs, Ca, Mg, and Mo. The catalytic activity of platinum increased with the increase in the electronegativity of additives and this was explained by assuming that the oxidation resistance of platinum under oxidizing conditions is enhanced with the increase in the additive electronegativity. Similarly, the same authors reported [11,12] that the propane oxidation activity on platinum is enhanced when the metal is supported on more acidic supports, probably because of a higher ability

\* Corresponding author. Tel.: +54-342-4555279; fax: +54-342-4531068.

E-mail address: [capesteg@fiqus.unl.edu.ar](mailto:capesteg@fiqus.unl.edu.ar) (C.R. Apesteguía).

to maintain the Pt metallic state. In contrast, Hubbard et al. [5] stated that the support acid strength does not have a major influence on propane oxidation activity. It is worth noting that in all these previous studies regarding the effect of support acidity on Pt activity for propane oxidation, authors did not use platinum supported on zeolitic materials.

In an attempt for developing more active Pt-based catalysts for lower-alkane combustion, we investigate in this work the deep oxidation of propane over Pt supported on zeolites. Specifically, we compare the propane oxidation activity of samples containing 0.32–0.44% Pt on MgO, Al<sub>2</sub>O<sub>3</sub> and zeolites KL, HY, ZSM5, and Beta. Results show that the propane oxidation turnover rate is more than two orders of magnitude higher on Pt/acid zeolites compared to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. This rate enhancement is essentially analyzed in terms of both support acidity and support capacity for adsorbing propane. The superior activity of Pt/zeolites for propane combustion is attributed to the zeolite ability for increasing the density of propane molecules adsorbed in the interfacial metal-support region.

## 2. Experimental

### 2.1. Catalyst preparation

Six Pt-supported catalysts of similar Pt contents were prepared. Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was made by incipient-wetness impregnation at 303 K of a high-purity  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (Cyanamid Ketjen CK300) with an aqueous solution of tetraamine platinum nitrate, Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa) for 6 h. The CK300 alumina has BET surface area ( $S_g$ ) of 180 m<sup>2</sup> g<sup>-1</sup>, pore volume of 0.49 cm<sup>3</sup> g<sup>-1</sup> and contains 50 ppm sulfur. The impregnated alumina was dried overnight at 393 K, then heated in air at 773 K for 4 h and finally reduced 4 h at 773 K in pure hydrogen. Three portions of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst were treated for 2 h in a 2% O<sub>2</sub>/N<sub>2</sub> mixture at 868, 883, and 893 K, respectively, in order to sinter the metallic fraction and then reduced 4 h at 773 K; the resulting sintered catalysts are identified here as Pt/Al<sub>2</sub>O<sub>3</sub>-1, Pt/Al<sub>2</sub>O<sub>3</sub>-2, and Pt/Al<sub>2</sub>O<sub>3</sub>-3, respectively. Pt/MgO was prepared following the same procedure described for Pt/Al<sub>2</sub>O<sub>3</sub>; the MgO support was obtained by rehydration of a commercial MgO (Carlo Erba, 99%) as described elsewhere [13]. Platinum supported on HY zeolite (Pt/HY) was prepared by adding Pt by ion exchange. The HY zeolite was in turn obtained by exchanging a commercial NaY zeolite (UOP-Y 54, Si/Al = 2.4) with ammonium acetate (Sigma, 99%) at 298 K. HY zeolite was treated with deionized water at 343 K for 12 h in a stirred batch reactor and then an aqueous solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> was added dropwise. The sample was kept at 343 K for 12 h and then filtered, washed thoroughly with deionized water, and dried at 373 K overnight. Finally, Pt/HY was heated in air at 0.2 K min<sup>-1</sup> from 298 up to 573 K and then reduced with flowing H<sub>2</sub> for 1 h at 673 K. Samples of Pt supported on zeolites Beta

(Zeocat PB, Si/Al = 25), ZSM5 (Zeocat Pentasil PZ-2/54, Si/Al = 20) and KL (commercial Tosoh zeolite) were prepared following the same procedure used for Pt/HY.

### 2.2. Catalyst characterization

The platinum dispersion ( $D_{Pt}$ ) was determined by chemisorption of hydrogen and oxygen (OC). The volumetric adsorption experiments were performed at 298 K in a conventional vacuum unit equipped with an MKS Baratron pressure gauge. Catalysts were reduced in H<sub>2</sub> at 673 K for 2 h and then outgassed 2 h at 773 K prior to performing gas chemisorption experiments. Hydrogen uptake was determined using the double isotherm method. After cooling to room temperature a first isotherm (primary isotherm) was drawn for measuring the total H<sub>2</sub> uptake. Then, and after 1 h of evacuation at room temperature, a second isotherm (secondary isotherm) was performed to determine the amount of weakly adsorbed H<sub>2</sub>. The amount of irreversibly held H<sub>2</sub> (HC)<sub>i</sub>, was calculated as the difference between total and weakly adsorbed H<sub>2</sub>. The pressure range of isotherms was 0–6.6 kPa. In the case of oxygen chemisorption, a single isotherm was performed for determining (OC) values since the amount of reversible oxygen at room temperature was negligible. Stoichiometric atomic ratios of (HC)<sub>i</sub>/Pt<sub>s</sub> = 1 and (OC)/Pt<sub>s</sub> = 1, where Pt<sub>s</sub> implies a Pt atom on surface, were used to calculate the platinum dispersion. Mean Pt crystallite sizes ( $\bar{d}_{Pt}$ , Å) were determined from chemisorption data by using site densities of  $1.12 \times 10^{15}$  sites cm<sup>-2</sup> of metal [14].

Acid site densities were determined by using temperature programmed desorption (TPD) of NH<sub>3</sub>. Samples (200 mg) were treated in He ( $\sim 60$  cm<sup>3</sup> min<sup>-1</sup>) at 773 K for 1.5 h and exposed to a 1.01% NH<sub>3</sub>/He stream at 373 K until surface saturation. Weakly adsorbed NH<sub>3</sub> was removed by flowing He at 60 cm<sup>3</sup> min<sup>-1</sup> for 0.5 h. Temperature was then increased to 823 K at 10 K min<sup>-1</sup>, and the NH<sub>3</sub> concentration in the effluent was measured by mass spectrometry (MS) in a Baltzers Omnistar unit.

Propane uptakes were measured at 298 K and 0.8 kPa in a conventional vacuum equipment. Samples were treated in air at 573 K for 0.5 h, then outgassed at this temperature for 1 h and finally cooled in vacuum to room temperature prior to performing the propane adsorption experiments.

Platinum loadings were measured by atomic absorption spectrometry. Total surface areas ( $S_g$ ) were measured by N<sub>2</sub> physisorption at 77 K using a Quantachrome Nova-1000 sorptometer and BET analysis methods.

### 2.3. Catalytic tests

The oxidation of propane (AGA, 99.5%) was carried out at 101.3 kPa in a fixed-bed tubular reactor (Pyrex, 0.8 cm i.d.). Catalyst samples were held as a thin layer above a plug of acid-washed quartz wool. Temperatures were measured using a K type thermocouple placed into the catalyst

bed. Samples were sieved and fraction 0.35–0.42 mm was separated and loaded to the reactor. Zeolite powders were first pressed and compacted, and then crushed and screening to the desired size. In standard runs, catalyst loadings ( $W$ ) of 0.3 g, contact times ( $W/F_p^0$ ) of 58 g catalyst h mol<sup>-1</sup> propane, and gas flow rate (GHSV) of 1007 cm<sup>3</sup> (STP) g<sup>-1</sup> min<sup>-1</sup>, were used. Propane was fed in concentration of 0.8% in a 10% O<sub>2</sub>/N<sub>2</sub> mixture. On-line chromatographic analysis was performed using a gas chromatograph Shimadzu GC-8A equipped with a flame ionization detector and 23% SP-1700 Supelco packed columns. Before gas chromatographic analysis, the reaction products were separated and carbon dioxide converted to methane by means of a methanation catalyst (Ni/Kieselghur) operating at 673 K. The presence of water in the products was verified but not quantified. Carbon monoxide was never detected in the effluent. Before catalytic measurements, all the catalysts were reduced in hydrogen at 673 K for 1 h and then cooled to the desired temperature. Two experimental procedures were used for catalyst testing. Deep propane oxidation was studied by obtaining curves of hydrocarbon conversion ( $X$ ) as a function of temperature (light-off curves). The temperature was raised by steps of about 20 K, from 373 to 850 K. More fundamental differential reactor experiments (less than 10% conversion) were performed at constant temperature. The products were sampled at 5 min intervals using an automated sampling valve. In steady-state rate measurements, diffusional limitations were ruled out by varying particle sizes and contact times between 0.15–0.49 mm and 10–150 g h mol<sup>-1</sup>, respectively.

### 3. Results

#### 3.1. Catalyst characterization

The main characteristics of the samples are shown in Table 1. The amount of Pt was between 0.32 and 0.44% on all the catalysts. The metallic dispersions shown in Table 1 were determined by H<sub>2</sub> chemisorption; selected samples were also characterized by O<sub>2</sub> chemisorption. In all the cases the

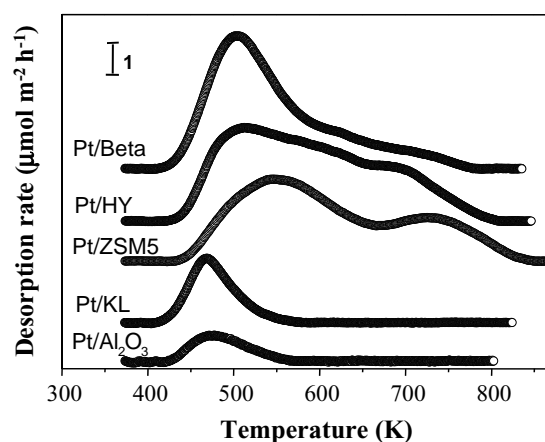


Fig. 1. TPD profiles of NH<sub>3</sub> on Pt-supported samples. NH<sub>3</sub> adsorption at 373 K, 10 K min<sup>-1</sup> heating rate.

difference between  $D_{Pt}$  values determined by both methods was lower than 5%. Table 1 shows that the platinum dispersion on fresh catalysts varied between 29 and 53%, excepting for Pt/KL ( $D_{Pt} = 71\%$ ). Fresh Pt/Al<sub>2</sub>O<sub>3</sub> ( $D_{Pt} = 53\%$ ) was treated at high temperatures as previously described to obtain three sintered samples: Pt/Al<sub>2</sub>O<sub>3</sub>-1 ( $D_{Pt} = 42\%$ ), Pt/Al<sub>2</sub>O<sub>3</sub>-2 ( $D_{Pt} = 22\%$ ), and Pt/Al<sub>2</sub>O<sub>3</sub>-3 ( $D_{Pt} = 19\%$ ). It was verified that sintering treatments did not change the alumina surface area ( $S_g = 180 \text{ m}^2 \text{ g}^{-1}$ ).

The sample acid properties were probed by TPD of NH<sub>3</sub> preadsorbed at 373 K (Fig. 1). The amount of NH<sub>3</sub> desorbed from Pt/MgO was negligible. The NH<sub>3</sub> TPD profiles on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/KL show that NH<sub>3</sub> desorbs in a band between 425 and 550 K. As expected, the NH<sub>3</sub> TPD profiles of Fig. 1 qualitatively show that acid zeolites contain a higher density of stronger acid sites compared to zeolite KL or Al<sub>2</sub>O<sub>3</sub> supports. In fact, on Pt supported on acid zeolites, NH<sub>3</sub> desorbs in two or three broad bands, from 425 to 800 K. The NH<sub>3</sub> surface densities were obtained by deconvolution and integration of the TPD traces and are presented in Table 1. The total adsorbed NH<sub>3</sub> surface densities on Pt/HY (0.86 μmol m<sup>-2</sup>), Pt/ZSM5 (0.89 μmol m<sup>-2</sup>), and Pt/BEA (1.02 μmol m<sup>-2</sup>) were significantly higher

Table 1  
Characteristics of the catalysts used in this work

Catalyst	$S_g$ (m <sup>2</sup> g <sup>-1</sup> )	Pt loading (%)	Pt dispersion $D_{Pt}$ (%)	Surface Pt concentration (μmol Pt <sub>s</sub> g <sup>-1</sup> catalyst)	Mean Pt particle size $\bar{d}_{Pt}$ (Å)	Propane uptake <sup>a</sup> (μmol m <sup>-2</sup> )	NH <sub>3</sub> TPD (μmol m <sup>-2</sup> )
Pt/MgO	140	0.40	35	7.18	24.2	0.011	n.d. <sup>b</sup>
Pt/Al <sub>2</sub> O <sub>3</sub>	180	0.33	53	8.96	16.0	0.035	0.11
Pt/Al <sub>2</sub> O <sub>3</sub> -1	180	0.33	42	7.10	20.1	–	–
Pt/Al <sub>2</sub> O <sub>3</sub> -2	180	0.33	22	3.72	38.4	–	–
Pt/Al <sub>2</sub> O <sub>3</sub> -3	180	0.33	19	3.21	44.5	–	–
Pt/KL	290	0.44	71	16.01	11.9	0.42	0.19
Pt/HY	440	0.32	40	6.56	21.1	0.82	0.86
Pt/ZSM5	400	0.36	30	5.54	28.2	1.02	0.89
Pt/Beta	560	0.33	29	4.91	29.2	0.90	1.03

<sup>a</sup> Propane uptakes measured at 298 K and  $P_p = 0.8 \text{ kPa}$ .

<sup>b</sup> n.d.: not detected.

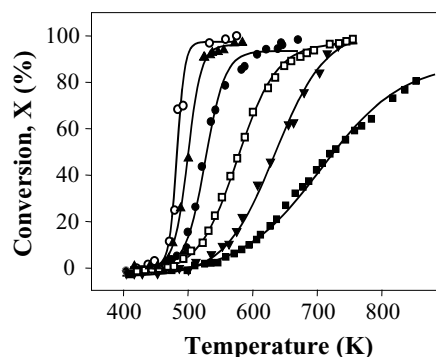


Fig. 2. Light-off curves for propane combustion. Pt/Beta (○); Pt/ZSM5 (▲); Pt/HY (●); Pt/KL (□); Pt/Al<sub>2</sub>O<sub>3</sub> (▼); Pt/MgO (■).  $W/F_P^0 = 58 \text{ g h mol}^{-1}$ ; propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3;  $P = 101.3 \text{ kPa}$ .

compared to those on Pt/Al<sub>2</sub>O<sub>3</sub> (0.11  $\mu\text{mol m}^{-2}$ ) and Pt/KL (0.19  $\mu\text{mol m}^{-2}$ ).

The sample propane uptake capacity was determined at room temperature for a propane partial pressure of 0.8 kPa, which was the hydrocarbon pressure used in catalytic tests. Results are shown in Table 1. The highest areal propane uptakes were measured on Pt/acid zeolites. Specifically, propane adsorption on Pt/acid zeolites was about 20 times higher than on Pt/MgO and Pt/Al<sub>2</sub>O<sub>3</sub>, but only about two times higher than on Pt/KL.

### 3.2. Catalytic tests

Fig. 2 shows the  $X$  versus  $T$  curves obtained for all the samples, excepting sintered Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. The light-off curves show that the activity for propane combustion follows the order Pt/MgO < Pt/Al<sub>2</sub>O<sub>3</sub> < Pt/KL < Pt/HY < Pt/ZSM5 < Pt/Beta. Most active platinum catalysts give rise to sharp light-off curves shifted to lower temperatures. To quantitatively compare catalyst activities, we measured from light-off curves the value of the temperature at  $X = 50\%$ ,  $T^{50}$  (Table 2). Repeat profiles carried out with fresh Pt/Al<sub>2</sub>O<sub>3</sub> sample confirmed the stability of the light-off temperature. Table 2 shows that  $T^{50}$  decreased from 715 (MgO) to 485 K (Pt/Beta).

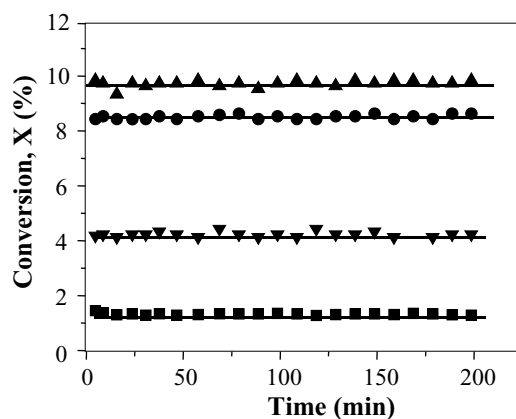


Fig. 3. Propane conversion as a function of time. Pt/ZSM5 (▲),  $W/F_P^0 = 1.8 \text{ g h mol}^{-1}$ ; Pt/HY (●),  $W/F_P^0 = 1.4 \text{ g h mol}^{-1}$ ; Pt/Al<sub>2</sub>O<sub>3</sub> (▼);  $W/F_P^0 = 58$ ; Pt/MgO (■),  $W/F_P^0 = 58 \text{ g h mol}^{-1}$ .  $T = 533 \text{ K}$ ; propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3;  $P = 101.3 \text{ kPa}$ .

Propane oxidation was also carried out on Pt catalysts at constant temperature (533 K). In all the cases, the initial conversion was lower than 10% and the reaction was kinetically controlled. Fig. 3 shows the  $X$  versus time plots obtained on several samples of Table 1 at 533 K, and typically illustrates the time-on-stream behavior of the catalysts during the reaction. Propane conversion remained approximately constant in all the cases, thereby indicating that no significant catalyst deactivation takes place on stream.

From  $X$  versus time curves we determined the propane combustion rates ( $r$ , mol propane  $\text{h}^{-1} \text{g}_{\text{Pt}}^{-1}$ ) and turnover frequencies (TOF,  $\text{h}^{-1}$ ) at 533 K; the values are shown in Table 2. The TOF values on Pt-supported catalysts increased following the same trend as determined from light-off curves in Fig. 1. But it is worth noting that the intrinsic activity of Pt for propane combustion on acid zeolites HY, ZSM5, and Beta was about two or three orders of magnitude higher than on MgO or Al<sub>2</sub>O<sub>3</sub>.

The effect of metal dispersion on the intrinsic Pt activity for propane oxidation was investigated by measuring propane combustion rates on four Pt/Al<sub>2</sub>O<sub>3</sub> samples containing the same amount of Pt but different mean

Table 2  
Catalytic results

Catalyst	Light-off curves <sup>a</sup> , $T^{50}$ (K)	Kinetically-controlled catalytic tests					
		$r^b$ (mol $\text{h}^{-1} \text{g}_{\text{Pt}}^{-1}$ )	TOF <sup>b</sup> ( $\text{h}^{-1}$ )	Reaction orders		$E_a$ (kcal $\text{mol}^{-1}$ )	$A$ ( $\text{h}^{-1} \text{kPa}^{-(1+\beta)}$ )
				$\alpha$	$\beta$		
Pt/MgO	715	0.05	30	0.92	0	8.8	$2.93 \times 10^5$
Pt/Al <sub>2</sub> O <sub>3</sub>	630	0.22	83	1.15	0	17.0	$8.28 \times 10^8$
Pt/KL	580	5.14	1400	0.98	-0.20	19.0	$2.50 \times 10^{11}$
Pt/HY	525	17.72	9000	0.96	-0.75	21.0	$2.72 \times 10^{13}$
Pt/ZSM5	500	15.34	10000	1.05	-0.71	27.5	$2.36 \times 10^{16}$
Pt/Beta	485	56.43	39300	1.02	-1.08	29.0	$8.10 \times 10^{17}$

<sup>a</sup>  $W/F_P^0 = 58 \text{ g h mol}^{-1}$ ; propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3;  $P = 101.3 \text{ kPa}$ .

<sup>b</sup> Propane oxidation rates determined at:  $T = 533 \text{ K}$ , propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3,  $P = 101.3 \text{ kPa}$ .

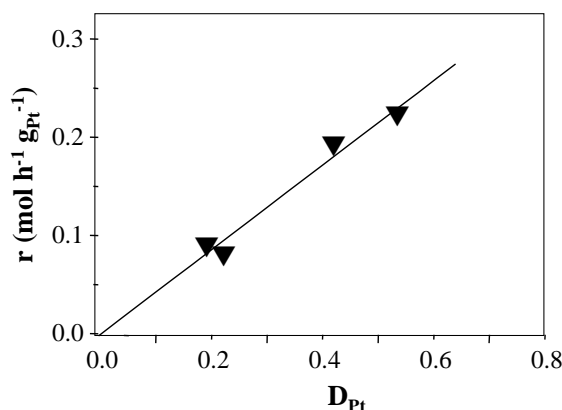


Fig. 4. Propane combustion rate as a function of metallic dispersion. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts;  $T = 533$  K; propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3;  $P = 101.3$  kPa;  $W/F_p^0 = 58$  g h mol<sup>-1</sup>.

Pt crystallite sizes ( $\bar{d}_{Pt}$ ) (Table 1, samples Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>-1, Pt/Al<sub>2</sub>O<sub>3</sub>-2, and Pt/Al<sub>2</sub>O<sub>3</sub>-3). Specifically,  $\bar{d}_{Pt}$  was varied between 16.0 and 44.5 Å. Propane combustion rates determined on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were represented as a function of Pt dispersion in Fig. 4. A linear plot was obtained thereby showing that propane combustion on Pt/Al<sub>2</sub>O<sub>3</sub> is a structure insensitive reaction.

The reaction orders on all the catalysts were determined by considering for propane combustion rate a power-law rate equation:

$$r = k(P_P^0)^\alpha (P_{O_2}^0)^\beta \quad (1)$$

where  $P_P^0$  and  $P_{O_2}^0$  are the partial pressures of propane and oxygen in the feed, respectively. The  $\alpha$  values were measured by varying the propane partial pressure between 0.5 and 1.1 kPa at a fixed oxygen pressure (9.9 kPa). Similarly, reaction order  $\beta$  was obtained by varying  $P_{O_2}^0$  between 4.9 and 20.5 kPa while keeping  $P_P^0$  at 0.8 kPa. Reaction orders  $\alpha$  and  $\beta$  were determined graphically from logarithmic plots representing the  $r$  values as a function of  $P_P^0$  and  $P_{O_2}^0$ , respectively (Fig. 5); the obtained values are shown in Table 2. On all the catalysts, the reaction order with respect to propane was close to one, while the reaction order in oxygen was about zero on Pt/MgO and Pt/Al<sub>2</sub>O<sub>3</sub> and negative on Pt

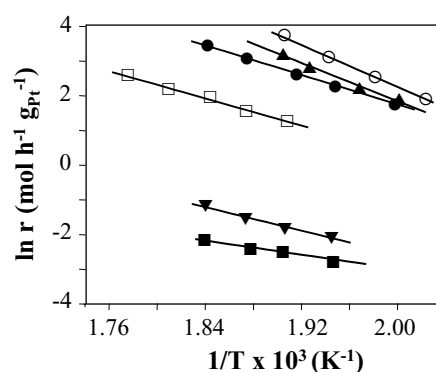


Fig. 6. Arrhenius plots for determining  $E_a$  (apparent activation energy) and  $A$  (preexponential factor). Catalysts: Pt/Beta (○); Pt/ZSM5 (▲); Pt/HY (●); Pt/KL (□); Pt/Al<sub>2</sub>O<sub>3</sub> (▼); Pt/MgO (■).  $P = 101.3$  kPa;  $W/F_p^0 = 58$  g h mol<sup>-1</sup>; propane:O<sub>2</sub>:N<sub>2</sub> = 0.8:9.9:89.3.

supported on zeolites. The absolute value of  $\beta$  increased with increasing zeolite acidity.

The apparent activation energy ( $E_a$ ) and pre-exponential factor  $A$  of propane combustion on all the catalysts were obtained via an Arrhenius-type function, by plotting  $\ln r$  values as a function of  $1/T$ . We obtained  $E_a$  from the slope of the resulting linear plots (Fig. 6), and from the ordinate values at  $1/T = 0$  we determined pre-exponential factors  $A$ . Results are shown in Table 2. It is observed that the activation energy increased with the catalyst activity: the higher the catalyst activity, the higher the  $E_a$  value. A similar trend was found between pre-exponential factors  $A$  and catalyst activity: the most active catalyst shows the highest  $A$  value. In order to verify if the experimental data obey a Cremer–Constable relation [15,16]:

$$\ln A = mE_a + c \quad (2)$$

we plotted in Fig. 7 the  $\ln A$  values as a function of  $E_a$ . A linear plot was obtained thereby indicating that a compensation phenomenon took place. Compensation is often observed when the reactant chemisorption is weaker, since the resulting lower coverage are temperature dependent and sensitive to many variables such as catalyst composition. Under these conditions, reaction orders would be greater than

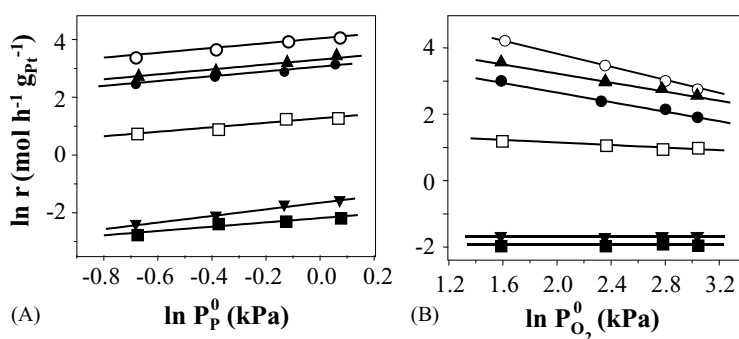


Fig. 5. Dependence of propane oxidation upon propane (A) and oxygen (B) partial pressures. Catalysts: Pt/Beta (○); Pt/ZSM5 (▲); Pt/HY (●); Pt/KL (□); Pt/Al<sub>2</sub>O<sub>3</sub> (▼); Pt/MgO (■).  $T = 533$  K;  $P = 101.3$  kPa;  $W/F_p^0 = 58$  g h mol<sup>-1</sup>.

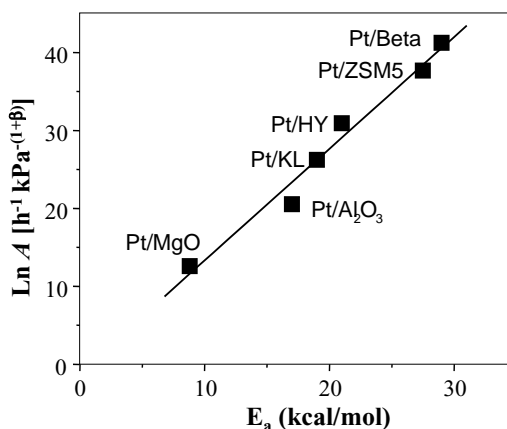


Fig. 7. Constable plot for propane combustion on platinum-supported catalysts.

zero. In most cases, compensation has been observed for first order reactions [17], as we determined here for propane combustion.

The existence of a compensation phenomenon is also qualitatively consistent with the  $X$  versus  $T$  curve shapes shown in Fig. 2. In fact, the design equation of a plug-flow integral reactor is:

$$\frac{W}{F_p^0} \left( \frac{\text{g catalyst h}}{\text{mol}} \right) = \int \frac{dX}{w_{\text{Pt}} r_{(X,T)}} \quad (3)$$

where  $w_{\text{Pt}}$  (g Pt g<sup>-1</sup> catalyst) is the metallic fraction in weight basis.

In our case, when  $\alpha = 1$  and  $\beta = 0$ ,  $r_{(X,T)}$  is:

$$r_{(X,T)} = A e^{-(E_a/RT)} C_p^0 (1 - X) \quad (4)$$

where  $C_p^0$  is the propane concentration in the feed.

Replacing  $r_{(X,T)}$  from (4) in (3) and integrating we obtain the  $X = f(T)$  function:

$$X = 1 - \left\{ \exp \left[ -qA \exp \left( \frac{-E_a}{RT} \right) \right] \right\} \quad (5)$$

where

$$q = \frac{W}{F_p^0} C_p^0 w_{\text{Pt}}$$

According to Eq. (5), when  $E_a$  increases the  $X$  versus  $T$  curve is shifted to higher temperatures without changing the sigmoidal curve shape; i.e. the catalyst becomes less active. In contrast, the light-off curve becomes sharper and is shifted to lower temperatures by increasing  $A$ . Qualitatively, the evolution of the  $X$  versus  $T$  curves in Fig. 2 reflects the behavior predicted by Eq. (5) when  $A$  increases, in spite of the simultaneous increasing of the apparent activation energy. This is typical of the usual positive compensation in which the trend of  $\ln A$  with  $E_a$  is sympathetic.

## 4. Discussion

Propane oxidation turnover rates on Pt/acid zeolites were more than two orders of magnitude higher than on Pt/Al<sub>2</sub>O<sub>3</sub> (Table 2). On Pt-based catalysts, the activity for hydrocarbon combustion may be strongly dependent on the mean metal particle size. For example, we have found [18,19] that turnover rates for benzene and cyclopentane oxidations on Pt/Al<sub>2</sub>O<sub>3</sub> increase more than one order of magnitude when  $\bar{d}_{\text{Pt}}$  is increased from about 15–50 Å. However, we do not observe any significant change in the TOF value for propane oxidation with increasing Pt particle size (Fig. 4). In agreement with these results, it has been reported [20] that the turnover rates for the total oxidation of C<sub>1</sub> to C<sub>4</sub> *n*-alkanes on Pt/Al<sub>2</sub>O<sub>3</sub> decrease only slightly with decreasing metallic dispersion. It seems that the rate-determining step in the alkane oxidation reaction mechanism, i.e. the abstraction of the first hydrogen on the adsorbed alkane molecule [21–23], is not a demanding reaction on Pt. The differences in the propane oxidation turnover rates shown in Table 2 can not be explained therefore by any change of the Pt crystallite size.

Recently, Yazawa et al. [11,12,24] studied the propane combustion on Pt/MgO, Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/ZrO<sub>2</sub>, Pt/SiO<sub>2</sub>, Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Pt/SO<sub>4</sub>-ZrO<sub>2</sub> catalysts and reported that the intrinsic activity of Pt increases with the acid strength of support materials. In basis of catalyst characterization results obtained by EXAFS spectroscopy, they postulated that under oxidizing conditions the oxidation resistance of platinum is enhanced on electrophilic supports, thereby increasing the Pt combustion activity. However, Hubbard et al. [5] studied the effect of support material (namely alumina, zirconia, and silica) and sulfation on propane oxidation activity over platinum and concluded that the support acid strength is not the only important factor on propane combustion activity. Similarly, Burch et al. [6] studied the combustion of propane on Pt supported on sulfated and fluorinated aluminas and reported that attempts to correlate the catalyst activity with the total acidity of the support were unsuccessful. Our light-off curves in Fig. 2 show that the activity of Pt-based catalysts for propane combustion increases following approximately the increase in the support acidity (Table 1). Nevertheless, quantitative results obtained in kinetically-controlled catalytic tests (Table 2) show that in the propane oxidation turnover rate trend

$$\begin{aligned} \text{Pt/MgO} &< \text{Pt/Al}_2\text{O}_3 \ll \text{Pt/KL} < \text{Pt/HY} \\ &\leq \text{Pt/ZSM5} < \text{Pt/Beta} \end{aligned}$$

a drastic TOF enhancement is verified from Pt/Al<sub>2</sub>O<sub>3</sub> to Pt/KL, despite that the NH<sub>3</sub> TPD characterization shows that Al<sub>2</sub>O<sub>3</sub> and zeolite KL supports exhibit similar acid strength (Fig. 1 and Table 1). It is then apparent that the abrupt increase of the Pt activity for propane oxidation observed on Pt/KL can not be explained only in terms of density of surface acid sites.

On the other hand, we observe that the reaction order with respect to oxygen is about zero on both Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/MgO, and negative on Pt/zeolites (Table 2). These results are consistent with previous works reporting that lower-alkanes oxidation is order zero or negative on Pt-based catalysts [11,12,25]. Propane adsorption on Pt is energetically competitive with oxygen [20] and the interaction between the two competitively adsorbed reactants explains in a Langmuir–Hinshelwood mechanism the reaction inhibition by O<sub>2</sub>, depending on the conditions used. But it should be noted that our results show that the negative order with respect to oxygen increases with increasing support acidity (Tables 1 and 2) and this is not consistent with the interpretation that Pt on electrophilic supports has the higher oxidation resistance. In fact, if the effect of the acid supports is to prevent Pt from oxidation it is expected that the inhibition by O<sub>2</sub> would decrease with the support acid strength. In summary, the general picture emerging from the above results is that the support acidity is not the major contributing factor for explaining the drastic propane oxidation turnover rate enhancement determined on Pt/zeolites as compared to Pt/Al<sub>2</sub>O<sub>3</sub>.

Results in Table 1 show that the areal propane uptake on Pt/KL is one order of magnitude higher than on Pt/Al<sub>2</sub>O<sub>3</sub>. Propane adsorption is still higher on Pt/acid zeolites. A drastic increase of the density of propane adsorbed species under reaction may promote the alkane oxidation rate and probably explains the high TOF values observed on Pt/zeolites. Specifically, we propose that on Pt/zeolites the propane species adsorbed in the metal-oxide interfacial region react with oxygen spilled-over from Pt. This additional reaction pathway would be kinetically significant only on Pt/zeolites because of the high density of propane species adsorbed on the support. The higher TOF values for propane combustion determined on Pt/HY, Pt/ZSM5, and Pt/Beta as compared to Pt/KL is consistent with the fact that the propane uptake on acid zeolites was higher than on zeolite KL. Fig. 8 shows a simplified scheme representing the proposed reaction pathways for the combustion of propane on Pt/zeolites. In the main oxidation mechanism on platinum (Fig. 8A) the rate-determining step is the dissociative chemisorption of the alkane on Pt with the breakage of the weakest C–H bond followed by its interaction with oxygen atoms adsorbed on adjacent sites. In a parallel oxidation pathway (Fig. 8B), propane is adsorbed and activated on

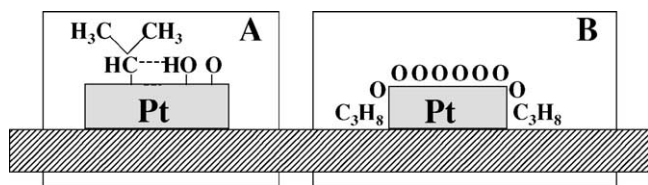


Fig. 8. Proposed propane oxidation pathways on Pt-based catalysts. (A) Main reaction pathway on platinum; (B) additional reaction pathway on Pt/zeolites.

surface sites in the metal-oxide interfacial region and reacts with oxygen spilled-over from platinum. Propane oxidation via this later mechanism will be promoted by increasing the density of adsorbed propane molecules in the interfacial region. Thus, the superior performance of Pt/acid zeolites for propane oxidation is consistent with the fact that acid zeolites exhibit the highest propane uptake capacities of the catalysts investigated in this work. A similar model considering that the overall activity can be separated into that from the metal surface and that from the interfacial region has been proposed for explaining the aromatic hydrocarbon hydrogenation rate enhancement obtained on Pt supported on acid materials as compared to Pt/SiO<sub>2</sub> catalysts [26,27]. Finally, the assumption that propane is oxidized via a contributing pathway in perimeter sites of the metal-support interface is also qualitatively consistent with the occurrence of a compensation effect. In fact, the proposed additional oxidation pathway is an activated reaction involving oxygen spilled-over from platinum and would increase then the apparent activation energy of the global reaction rate. However, this  $E_a$  increase will be kinetically compensated by a concomitant drastic augmentation of frequency factor  $A$  caused by the increase in the density of propane adsorbed molecules.

## 5. Conclusions

On the Pt-based catalysts used in this work, propane combustion is first order with respect to propane, and zero or negative order with respect to oxygen, shows a positive compensation relation, and is not a structure sensitive reaction. Turnover rates for propane oxidation follow the order: Pt/MgO < Pt/Al<sub>2</sub>O<sub>3</sub> << Pt/KL < Pt/HY ≤ Pt/ZSM5 < Pt/Beta. Pt/acid zeolites are the most active catalysts, but a drastic activity enhancement is verified from Pt/Al<sub>2</sub>O<sub>3</sub> to Pt/KL, despite that alumina and zeolite KL supports exhibit similar acid strength. The support acidity does not play a major role on propane combustion activity.

Propane uptakes on Pt/zeolites are more than one order of magnitude higher than on Pt/Al<sub>2</sub>O<sub>3</sub> and a drastic increase in the density of propane adsorbed species may explain the superior combustion activity obtained on Pt/zeolites. We propose that the increase in the concentration of propane adsorbed molecules turns kinetically significant an additional oxidation pathway occurring in the metal-support interface between adsorbed propane and the spilled-over oxygen from platinum. Propane combustion on Pt-supported catalysts would proceed then via two simultaneous mechanisms, i.e. the main oxidation pathway on platinum and a contributing oxidation pathway on the metal-oxide interfacial region. This later oxidation mechanism is only significant on Pt/zeolites because of the ability of zeolites for drastically increasing the density of adsorbed propane molecules in the interfacial region.

## Acknowledgements

The authors thank the Universidad Nacional del Litoral, Santa Fe (CAID 2002 20-137) and CONICET (Argentina) for the financial support of this work.

## References

- [1] J.J. Spivey, *Ind. Eng. Chem. Res.* 26 (1987) 2165.
- [2] K.T. Chuang, S. Cheng, S. Tong, *Ind. Eng. Chem. Res.* 31 (1992) 2466.
- [3] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, *J. Catal.* 122 (1990) 280.
- [4] F.H. Ribeiro, M. Chow, R.A. Dalla Beta, *J. Catal.* 146 (1994) 277.
- [5] C.P. Hubbard, K. Otto, H.S. Gandhi, K.Y. Ng, *J. Catal.* 144 (1993) 484.
- [6] R. Burch, E. Halpin, M. Hayes, K. Ruth, J.A. Sullivan, *Appl. Catal. B: Environ.* 19 (1998) 199.
- [7] A.F. Lee, K. Wilson, R. Lambert, C.P. Hubbard, R.G. Hurley, R.W. McCabe, H.S. Gandhi, *J. Catal.* 184 (1999) 491.
- [8] A. Hinz, M. Skoglundh, E. Fridell, A. Andersson, *J. Catal.* 201 (2001) 247.
- [9] Y. Yasawa, H. Yoshida, S. Komai, T. Hattori, *Appl. Catal. A: Gen.* 233 (2002) 113.
- [10] H. Wu, L. Liu, S. Yang, *Appl. Catal. A: Gen.* 211 (2001) 159.
- [11] Y. Yazawa, N. Kagi, S. Komai, A. Satsuma, Y. Murakami, T. Hattori, *Catal. Lett.* 72 (2001) 157.
- [12] Y. Yazawa, H. Yoshida, T. Hattori, *Appl. Catal. A: Gen.* 237 (2002) 139.
- [13] J.I. Di Cosimo, V. Díez, C.R. Apesteguía, *Appl. Catal.* 137 (1996) 149.
- [14] L. Spenadel, M. Boudart, *J. Phys. Chem.* 64 (1960) 204.
- [15] F.H. Constable, *Proc. R. Soc. (Lond.)* 108 (1925) 355.
- [16] E. Cremer, *Z. Phys. Chem.* 144 (1929) 231.
- [17] G.C. Bond, M.A. Keane, H. Kral, J.A. Lercher, *Catal. Rev. Sci. Eng.* 42 (3) (2000) 323.
- [18] T.F. Garetto, C.R. Apesteguía, *Catal. Today* 62 (2–3) (2000) 189.
- [19] T.F. Garetto, C.R. Apesteguía, *Appl. Catal. B: Environ.* 32 (1–2) (2001) 83.
- [20] Y.Y. Yao, *Ind. Eng. Chem. Prod. Res. Dev.* 19 (1980) 293.
- [21] L. Hiam, H. Wise, S. Chaikin, *J. Catal.* 9 (1968) 272.
- [22] M. Aryafar, F. Zaera, *Catal. Lett.* 48 (1997) 173.
- [23] T.F. Garetto, C. Apesteguía, in: A. Corma, F. Melo, S. Mendorioz, J.L.G. Fierro (Eds.), *Studies in Surface Science and Catalysis*, vol. 130, Elsevier, Amsterdam, 2000, p. 575.
- [24] Y. Yazawa, H. Yoshida, N. Takagi, N. Kagi, S. Komai, A. Satsuma, Y. Murakami, T. Hattori, in: A. Corma, F. Melo, S. Mendorioz, J.L.G. Fierro (Eds.), *Studies in Surface Science and Catalysis*, vol. 130, Elsevier, Amsterdam, 2000, p. 2189.
- [25] R. Burch, T.C. Watling, *J. Catal.* 169 (1997) 45.
- [26] S.D. Lin, M.A. Vannice, *J. Catal.* 143 (1993) 539.
- [27] S.D. Lin, M.A. Vannice, *J. Catal.* 143 (1993) 554.