Catalysis Letters 14 (1992) 57–64

Effect of lithium and residual nitrate species on platinum dispersion in Pt/Al_2O_3 catalysts

Fabio B. Passos *, Martin Schmal ☆
COPPE, Universidade Federal do Rio de Janeiro, Caixa Postal 68502, CEP 21941, Brasil

and

Roger Fréty
Institut de Recherches sur la Catalyse, CNRS, 2, Av. Albert Einstein,
69626 Villeurbanne Cedex, France

Received 5 December 1991; accepted 2 April 1992

The effect of lithium (ex $LiNO_3$) on the metallic dispersion of 0.8 wt% Pt/Al_2O_3 catalysts, prepared by different impregnation techniques, was investigated by temperature programmed reduction (TPR) and the frontal method of H_2 chemisorption. The temperature at which platinum precursor is reduced at a maximum rate (543 K) was not modified by 0.1 wt% lithium addition, whatever the preparation technique used. The dispersion values of platinum (70–90%), after reduction at 773 K, were slightly dependent on the preparation procedure. After the addition of 0.8 wt% lithium the TPR profile presented two well defind peaks and the dispersion values (20–50%), measured after reduction at 773 K, presented a significant decrease. The results are linked with the presence of residual nitrate ions, that had not been eliminated during calcination at 773 K in air, but had been decomposed under the reducing atmosphere of the TPR experiment.

Keywords: Pt/Al_2O_3; Li; NO_x; TPR; metal dispersion; hydrogen chemisorption; H_2–O_2 titration

1. Introduction

Alumina supported platinum catalysts are widely used in several hydrocarbon transformations. In the case of normal long-chain alkane dehydrogenation processes, Pt/Al_2O_3 catalysts are generally promoted with lithium [1,2]. Li–

---

* Present address: Departamento de Engenharia Quimica, Universidade Federal Fluminense, Rua Passos da Patria, 156, CEP 24210, Niteroi, Brasil.

☆ To whom correspondence should be addressed.

© J.C. Baltzer A.G. Scientific Publishing Company

Al_2O_3 interaction has been studied by several authors [3–5], who showed that there is a progressive lithium dissolution in the alumina. This dissolution can lead to the formation of a $LiAl_6O_8$ spinel [6,7], favouring the reducibility of alumina supported metals, like Cu or Ni. In the case of platinum catalysts, Bursian et al. [8] showed that the addition of alkaline promoters caused an increase in the aromatization activity and in the amount of the "soluble" platinum. The preceding results suggest that the presence of lithium in alumina could affect the reducibility of platinum.

The present work aims at studying the effect of lithium on:

(i) the reducibility of platinum precursors in Pt/Al_2O_3 catalysts,

(ii) the dispersion of the metallic phase after reduction at 773 K,

(iii) the role of residual NO_3^- ions introduced during impregnation of lithium compound.

2. Experimental

2.1. PREPARATION OF CATALYSTS

A commercial γ-Al_2O_3 (Harshaw Al 3996) with a BET surface area of 200 m^2 g^{-1}, was used as support. Pt/Al_2O_3 catalyst was prepared by incipient wetness impregnation of the support with an aqueous solution of H_2PtCl_6 (Riedel–de Haën), followed by drying at 393 K for 16 h, and calcination in air at 773 K for 2 h. Li/Al_2O_3 was prepared similarly with an aqueous solution of $LiNO_3$ (Riedel–de Haën).

Lithium addition to Pt/Al_2O_3 was performed by four distinct ways:

(a) Coimpregnation. The support was impregnated with an aqueous solution containing both H_2PtCl_6 and $LiNO_3$. Then, it was dried at 393 K for 16 h. The precursor prepared in this way will be termed $(Pt + Li)/Al_2O_3$.

(b) Pt/Al_2O_3 impregnated with lithium. After it had been impregnated with an aqueous solution of H_2PtCl_6 and dried at 393 K for 16 h, the support was reimpregnated with a $LiNO_3$ aqueous solution. After that, it was dried at 393 K for 16 h. This sample will be referred as $Li + (Pt/Al_2O_3)$.

(c) Li/Al_2O_3 impregnated with platinum. Similar procedure to the last one, but in a reverse order. This catalyst will be mentioned as $Pt + (Li/Al_2O_3)$.

(d) Reimpregnation with intermediate calcination step. The support was impregnated with a $LiNO_3$ aqueous solution, dried at 393 K for 16 h and calcined at 923 K for 2 h. After that, the impregnation with the H_2PtCl_6 aqueous solution was carried out, followed by drying at 393 K. These catalysts will be termed C-$Pt + (Li/Al_2O_3)$.

The dried samples obtained at the end of steps (a), (b), (c), and (d) were grounded to a mean particle diameter of 0.15 mm. Then, they were calcined in air at 773 K for 2 h. The prepared catalysts and their metal contents measured by atomic absorption spectroscopy are listed in table 1.

Table 1

Catalysts used in this study

Series	Catalysts	Composition (wt%)	
		Pt	Li
A	Pt/Al_2O_3	0.79	–
A	$(Pt+Li)/Al_2O_3$	0.84	0.10
A	$Pt+(Li/Al_2O_3)$	0.84	0.10
A	$Li+(Pt/Al_2O_3)$	0.90	0.10
B	Li/Al_2O_3	–	0.84
B	$(Pt+Li)/Al_2O_3$	0.84	0.80
B	$Pt+(Li/Al_2O_3)$	0.77	0.84
B	$Li+(Pt/Al_2O_3)$	0.79	0.78
C	$Pt+(Li/Al_2O_3)$	0.70	0.77

2.2. TEMPERATURE PROGRAMMED REDUCTION

The TPR apparatus and the relevant principles of this method have been described previously [9,10]. The precursors (1 g) were dehydrated at 393 K under flowing Ar, before being submitted to TPR. The reducing gas consisted of a 1.5% H_2 in Ar stream. The flow rate of the 1.5% H_2/Ar stream was 30 cm^3/min, and the temperature was raised to 773 K at a heating rate of 10 K/min.

2.3. CHEMISORPTION MEASUREMENTS

Hydrogen chemisorption and H_2–O_2 titration were performed at the same apparatus of the TPR. After the TPR experiment, the catalyst was flushed with an Ar gas flow at 773 K for 30 min, in order to remove any adsorbed H_2. Then, the sample was cooled to room temperature and the irreversible amount of adsorbed H_2 was measured by a frontal method [11]. The amount of hydrogen irreversibly adsorbed was used to calculate the dispersion of Pt, assuming the usual stoichiometry of $H/Pt^* = 1$, Pt^* being a platinum surface atom. The H_2–O_2 titration was carried out by treating the sample with an 5% O_2/He stream, purging with He, and at last, repeating the procedure of hydrogen chemisorption for the titration of adsorbed oxygen at the surface.

3. Results

3.1. TEMPERATURE PROGRAMMED REDUCTION

Fig. 1 presents the TPR profiles that were obtained and the reduction degrees of the catalysts. The TPR profile of the Pt/Al_2O_3 catalyst showed a

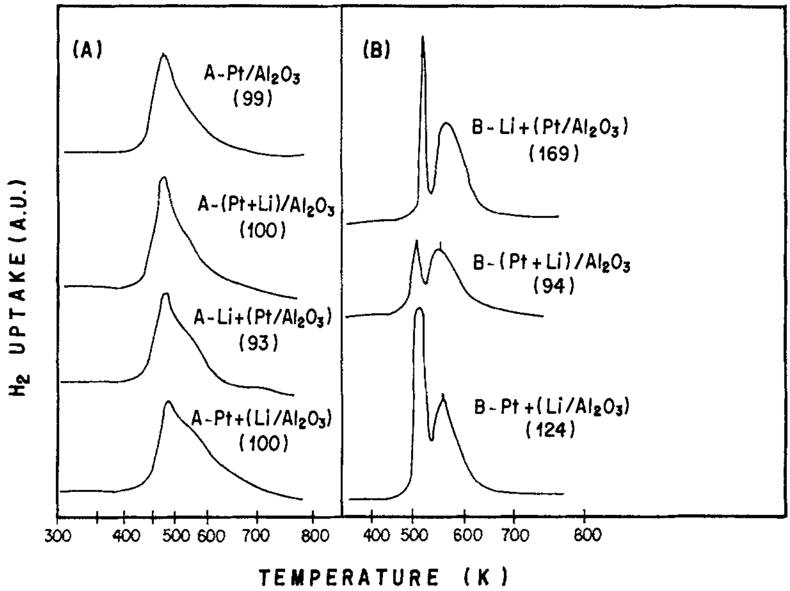

Fig. 1. TPR profiles for different catalysts of the A series (A) and B series (B). The number in parentheses gives the % reduction in the hypothesis that the reduction transforms Pt(IV) to Pt(0).

maximum reduction rate at 543 K, which corresponds to the reduction of a $[PtO_xCl_y]$ superficial complex, according to Lieske et al. [12]. The temperature of maximum reduction rate was similar for all catalysts of the A series. These catalysts also presented a systematic shoulder around 636 K, and appeared fully reduced, assuming the transformation of Pt(IV) to Pt(0).

The TPR profiles of catalysts of the B series, containing 0.8 wt% of Li, presented two peaks of maximum reduction rate, the first one close to 520–530 K and the second one around 580 K. The hydrogen uptakes of these catalysts appear rather irregular, B-Pt + (Li/Al_2O_3) and B-Li + (Pt/Al_2O_3) showing an experimental hydrogen uptake much higher than theoretically expected. The Li/Al_2O_3 sample, calcined at 773 K, showed a TPR peak near 736 K (fig. 2). No TPR peak appeared when the calcination temperature was 923 K. The TPR profile of C-Pt + (Li/Al_2O_3) showed, as the catalysts of the A series, a maximum rate at 543 K, but presented a different and pronounced shoulder around 600 K.

3.2. H_2 CHEMISORPTION

The amount of H_2 irreversibly adsorbed on different catalysts, reduced at 773 K are listed in table 2. The catalysts of the A series have rather high and similar dispersions. In the catalysts of the B series, the dispersions were much lower, although the difference between the catalysts is probably not really significant.

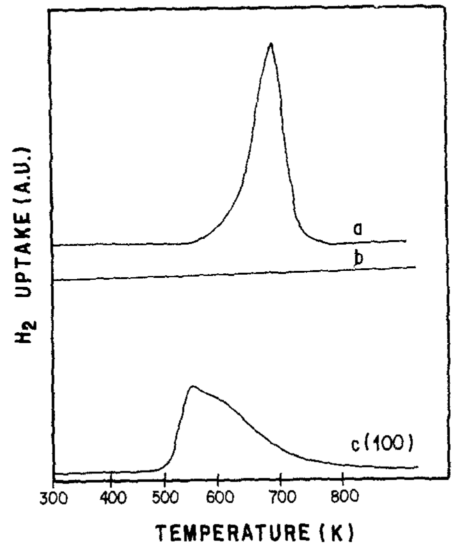

Fig. 2. TPR profile for Li/Al_2O_3 sample calcined at 773 K (a) and 923 K (b) and for C-Pt + (Li/Al_2O_3) catalyst (c). The number in parentheses gives the % reduction at the end of TPR.

The C-Pt + (Li/Al_2O_3) catalyst was highly dispersed (96%). Therefore, one can conclude that the lower dispersion in catalysts of B series are not simply due to the increase of lithium loading alone but they depended on the pretreatment of the precursors.

Some results of H_2/O_2 titration, also given in table 2, are in good agreement with the hydrogen chemisorption data, assuming the stoichiometry proposed by Benson and Boudart [13]. This point rules out any hydrogen chemisorption by lithium.

Table 2

Hydrogen chemisorption and oxygen–hydrogen titration results and dispersion calculated. Reduction of catalysts up to 773 K in the conditions of TPR experiments

Series	Catalysts	H_2 chemisorption ($\mu mol/g_{Pt}$)	H_2–O_2 titration ($\mu mol/g_{Pt}$)	Dispersion (%)
A	Pt/Al_2O_3	2060	5810	81
A	$(Pt+Li)/Al_2O_3$	1750	–	70
A	$Pt+(Li/Al_2O_3)$	2370	–	93
A	$Li+(Pt/Al_2O_3)$	2030	–	80
B	Li/Al_2O_3	–	–	–
B	$(Pt+Li)/Al_2O_3$	591	1610	23
B	$Pt+(Li/Al_2O_3)$	666	2000	26
B	$Li+(Pt/Al_2O_3)$	1130	–	44
C	$Pt+(Li/Al_2O_3)$	2460	–	96

4. Discussion

The TPR profile of Pt/Al_2O_3 was very similar to that presented by Lieske et al. [12], the peak at 543 K being attributed to the reduction of a superficial oxichloroplatinum complex $[PtO_xCl_y]_s$. This profile was not affected by the presence of lithium in the catalysts of the A series or for the catalyst prepared with intermediate calcination step (C-Pt + (Li/Al_2O_3)). Therefore, the superficial oxychloroplatinum complex formed during drying and calcination, due to the residual chlorine on the support, was not affected by the presence of a limited content of lithium.

Lithium oxide is not expected to be reduced in the present TPR conditions and no hydrogen uptake was observed after calcination at 923 K of B-Li/Al_2O_3. However, after a simple calcination at 773 K, a hydrogen uptake was observed around 736 K, during the TPR. We attributed this hydrogen uptake to the reduction of residual nitrate ions present in the sample, as bulk $LiNO_3$ is not fully decomposed to Li_2O before 870 K. Furthermore, after calcination at 773 K of B-Li/Al_2O_3 and for all catalysts of the B series, IR spectroscopy showed a narrow band close to 1380 cm^{-1}, typical of nitrate. This band was not observed in the catalysts of the A series containing Pt. Hence, we can assume that the presence of Pt helps the decomposition of a certain amount of NO_3^- during thermal treatment at 773 K. On the other hand, in the B series, due to the higher lithium content, a complete elimination of NO_3^- during the calcination at 773 K was not possible, and residual nitrate ions were eliminated during the reduction step. This fact can explain the new shape of TPR profile obtained for the B series and the high hydrogen consumption observed in two cases. Actually, the hydrogen amounts calculated for the catalysts of the B series are probably rather apparent, because some N_2, NH_3, NO_x formed during nitrate reduction could reach the thermal conductivity detector, and modify to some extent the general response during TPR. The reduction of nitrate ions occurs at a much lower temperature when platinum is present on the catalysts of the B series than with the Li/Al_2O_3: either a different localization of nitrate ions, or hydrogen activation on reduced platinum can explain this fact.

All the catalysts of the A series showed a shoulder around 600 K in their TPR profile. This shoulder cannot be explained by residual nitrate reduction, because the TPR profile of C-Pt + (Li/Al_2O_3) showed a shoulder at the same temperature range. We think that this shoulder could result either from the transition of $[PtO_xCl_y]$ to $[PtO_uCl_v]$ during the thermal process, or from the release of hydrogen in the gas phase: between 543 and 600 K, the metallic platinum surface formed during the initial steps of the TPR would be freed from chemisorbed hydrogen. According to the work of Levy and Primet [14] the TPD profiles of hydrogen, obtained on reduced Pt/Al_2O_3 catalysts under a 1% H_2/Ar stream, show maximum desorption rate around 550 K.

Summarizing, the presence of lithium does not affect significantly the reduction of $[PtO_xCl_y]$ precursor supported on alumina. On the other hand, residual nitrate ions are able to participate in the reduction, affecting both the TPR profiles and the hydrogen uptake during the TPR. Although the details of the interaction between nitrate or its reduction products are not known, the effect is quite clear. The presence of nitrate ions helps decreasing the platinum acessible area, as the dispersion of the metallic platinum is much lower when the TPR is performed with B series in the presence of nitrate ions. The loss of metallic area seems very closely related to the presence of nitrate ions during the reduction as its elimination by calcination at 923 K allows the occurrence of a very high dispersion of the metallic phase.

The reduction of nitrate ions during the TPR of some catalysts has been observed previously [15]. On the other side, the negative effect of residual chlorine on the catalytic properties of metallic catalysts [16–18] is well documented.

The presented results show that the modification of metal catalysts by an additive that can introduce nitrate ions during its deposition can change the reduction of the metal and decrease to a large extent its dispersion after reduction. Further measurements are being performed to see to what extent the catalytic activity is affected by such a situation.

5. Conclusions

The addition of 0.1 wt% of lithium to platinum alumina catalyst, followed by a calcination in air at 773 K, does not produce important modification in the reducibility of platinum precursor and in the final dispersion of the metal, after reduction at 773 K.

On the contrary, the addition of 0.8 wt% lithium modifies the TPR profile and induces an important drop in the metal dispersion. This drop in the platinum dispersion is due to the simultaneous reduction of residual nitrate ions with the platinum precursor.

Acknowledgement

This work has been supported by PRONAC (Programa Nacional de Catálise) and FINEP (Financiadora de Estudos e Projetos). RF is grateful to CNRS (Centre National de la Recherche Scientifique) for the authorization of a 15 months stay in Brazil. FBP acknowledges the support of DETEN S.A. during the work.

References

[1] S.K. Mart'yanova, N.A. Gaidai, M.M. Kostynkovskii, S.L. Kiperman and D.P. Shashkin, Kinet. Katal. 23 (1982) 907.
[2] E. Clippinger and B.F. Muslakey, US Patent 353143 (1970).
[3] W.H. Stork and G.T. Pott, J. Phys. Chem. 78 (1974) 2496.
[4] R.M. Levy and D.J. Bauer, J. Catal. 9 (1967) 76.
[5] V. Perrichon and M.C. Durupty, Appl. Catal. 42 (1988) 217.
[6] S. Narayan and K. Uma, J. Chem. Soc. Faraday Trans I 83 (1987) 733.
[7] S.I. Kozintsev, I.I Ugolev, G.A. Zhizhenko, S.V. Sinyakova, E.I. Savitskaya and N.S. Kozlov, Kinet. Katal. 28 (1987) 1257.
[8] N.R. Bursian, S.B. Kogan, G.M. Osmolovskii, B.G. Lyudkovskaya and Z.A. Davyodva, Kinet. Katal. 7 (1966) 556.
[9] P.N. da Silva, M. Guenin, C. Leclercq and R. Fréty, Appl. Catal. 54 (1989) 203.
[10] F.B. Noronha, M. Primet, R. Fréty and M. Schmal, Appl. Catal. 78 (1991) 125.
[11] R. Fréty, P.N. da Silva and M. Guenin, Appl. Catal. 58 (1990) 175.
[12] H. Lieske, G. Lietz, H. Spindler and J. Völter, J. Catal. 81 (1983) 8.
[13] J.E. Benson and M. Boudart, J. Catal. 4 (1965) 704.
[14] P.J. Levy and M. Primet, Appl. Catal. 70 (1991) 263.
[15] P. Arnoldy and J.A. Moulijn, J. Catal. 93 (1985) 38.
[16] T. Narita, H. Miura, T. Sugiyama, T. Matsuda and R.D. Gonzalez, J. Catal. 103 (1987) 492.
[17] K. Lu and J. Tatarchuk, J. Catal. 106 (1987) 176.
[18] T. LeVan, M. Bureau-Tardy, G. Bugli, G. Djega-Mariadassou, M. Che and G.C. Bond, J. Catal. 99 (1986) 449.