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Modification of platinum–alumina catalysts. Effect of the addition of lithium to platinum in the dehydrogenation of cyclohexane

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The modification of platinum–alumina catalysts by 0.1 wt% lithium does not affect to a large extent the dehydrogenating properties of platinum. However, when lithium is added to platinum through impregnation by nitrate salt in a higher content, residual nitrate species can remain on the catalyst surface, even after calcination at 773 K. These nitrate species can be co-reduced with the platinum precursor and be associated to a significant sintering of the platinum particles.

Keywords: modification; platinum–alumina catalyst; lithium; dehydrogenation; cyclohexane

1. Introduction

The catalytic dehydrogenation of normal paraffins, with chain length between C_9–C_{14}, to mono-olefins is the first step in the process of formation of linear alkyl benzenes, a starting material for obtaining biodegradable detergents [1].

This dehydrogenation is performed at about 723 K, using complex platinum based catalysts. These catalysts, not well studied in the literature, are modified by various promoters. Among them, tin and more recently indium [2] are probably modifying the metallic function, leading to platinum with reduced hydrogenolysis and better dehydrogenation properties. On the other hand, lithium is also added to the catalyst and is supposed to reduce the acidity of the alumina, and therefore the isomerization properties of the catalyst.

The interaction of lithium with alumina has been studied in the past. It has

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been shown that lithium can undergo a progressive dissolution in alumina, leading ultimately to $LiAl_5O_8$, a compound of spinel structure. Therefore, when transition metals that form easily spinel structure with alumina are supported on alumina modified by lithium, the transition metal spinel formation is inhibited and the whole reduction of the transition metal favored [3,4].

The effect of lithium addition on the dispersion of platinum in platinum–alumina catalysts has been studied to some extent, but the conclusions are slightly contradictory since increase, constancy and decrease of platinum dispersion were observed [5,6].

In a previous work [7], we have studied how the presence of lithium affects the reducibility and the dispersion of alumina supported platinum catalysts, calcined at 773 K. Independently of the sequence of impregnation, the reducibility and the metallic dispersion of 0.8 wt% platinum–alumina catalysts, containing 0.1 wt% lithium, were unchanged. By contrast, the addition of 0.8 wt% lithium to 0.8 wt% platinum–alumina solid has strongly modified the TPR profiles leading to a clear decrease of the platinum dispersion. Such situation has been attributed to residual nitrate species, introduced with lithium, not fully decomposed during the calcination step at 773 K, and coreduced with the platinum precursor.

This work presents the catalytic activity of such catalysts in the dehydrogenation of cyclohexane, to verify if the intrinsic dehydrogenation properties of the platinum were altered by the presence of lithium.

2. Experimental

Catalyst preparation. A commercial alumina (Harshaw Al3996) with a surface area of 200 m^2/g was used as carrier. Pt/Al_2O_3 and Li/Al_2O_3 samples were prepared by incipient wetness impregnation with hexachloroplatinum acid and lithium nitrate aqueous solutions, respectively. After drying at 393 K, the precursors were calcined in air at 773 K for 2 h. The addition of lithium and platinum to alumina was performed in three different ways, lithium being added before, simultaneously with or after platinum, to give $Pt + (Li/Al_2O_3)$, $(Pt + Li)/Al_2O_3$, and $Li + (Pt/Al_2O_3)$ samples, respectively. Details of the preparation are given in ref. [7]. The compositions of the calcined catalysts are listed in table 1.

Catalytic activity. The dehydrogenation properties of the various catalysts were measured at atmospheric pressure using cyclohexane conversion to benzene, in a dynamic differential reactor ($T = 540$ K, $p_{H_2}/p_{HC} = 13.2$, WSHV $= 170\ h^{-1}$). Before the reaction, the catalysts were reduced for 2 h, at 773 K and cooled to reaction temperature under pure hydrogen flow.

Catalyst characterization. Metallic areas were measured by irreversible hydrogen chemisorption, as described in ref. [7].

Table 1
Composition, catalytic properties and metallic area of different Pt–Li alumina catalysts

Catalyst	Series	Metal content (wt%)		Pt area (m^2/g-cat)	E_a (kJ/mol)	r[a]	TOF (s^{-1})
		Pt	Li				
Pt/Al_2O_3	A	0.79	–	1.56	158	17.8	1.2
Pt + (Li/Al_2O_3)	A	0.83	0.1	1.90	150	18.4	1.1
(Pt + Li)/Al_2O_3	A	0.84	0.1	1.44	120	15.5	1.2
Li + (Pt/Al_2O_3)	A	0.90	0.1	1.76	150	16.4	1.1
Pt/Al_2O_3	B	0.58	–	0.99	131	13.2	1.0
Pt + (Li/Al_2O_3)	B	0.71	0.1	1.05	134	13.6	1.2
(Pt + Li)/Al_2O_3	B	0.61	0.09	0.90	134	13.3	1.2
Li + (Pt/Al_2O_3)	B	0.60	0.09	0.99	140	13.4	1.1
Pt + (Li/Al_2O_3)	C	0.77	0.84	0.49	166	9.5	2.0
(Pt + Li)/Al_2O_3	C	0.84	0.84	0.49	125	9.8	2.3
Li + (Pt/Al_2O_3)	C	0.80	0.78	0.87	141	5.7	0.7
Pt + (Li/Al_2O_3)[b]	C	0.70	0.77	1.66	105	27.2	1.5

[a] r in mol/h g-Pt.

[b] Li/Al_2O_3 calcined at 923 K before impregnation with platinum.

3. Results and discussion

Table 1 gives the catalytic results expressed both as reaction rate (mol/h g-cat) and turnover frequency (TOF: s^{-1}), taking into account the metallic area calculated from hydrogen chemisorption. Apparent activation energies are also reported. For commodity, the catalysts are divided into three families, A, B and C, the atomic Li/Pt ratios being 3.5, 4.7 and 28.2, respectively.

Table 1 indicates that, whatever the catalyst, the apparent activation energy and TOF are rather constant, in agreement with the concept of cyclohexane hydrogenation being a "structure insensitive reaction" [8]. This is also in agreement with previous data concerning the platinum catalysts [8–11], although here platinum in the catalysts of the C series is probably slightly affected. Thus, the effect of lithium on platinum is, if any, rather limited.

Fig. 1 presents the reaction rate versus the metallic area. It shows that the catalysts become less active when the ratio Li/Pt increases, indicating that the relative increase in lithium leads to less accessible platinum area.

A final test was performed to verify if platinum is sintering or inhibited, in the absence of TEM data, by using a catalyst in which platinum was impregnated on lithium/alumina precalcined at 923 K. Table 1 shows that in this latter case, both the activity and the metallic area increased by a factor of 2. Calcination of Li/Al_2O_3 at 923 K has also induced a decrease of hydrogen consumption in TPR [7], basically due to the destruction of the residual nitrate species, easily reduced at

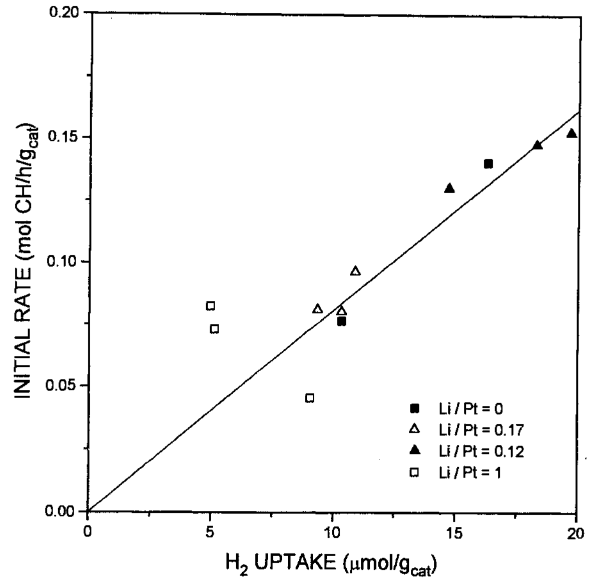

Fig. 1. Dehydrogenation of cyclohexane at 540 K.

about 500–550 K in the presence of platinum, and not eliminated during the calcination of the catalysts at 773 K. Through a mechanism not still known, the coreduction of nitrate species and platinum precursor led to a drop of the platinum area. This phenomenon has to be taken into account when preparing catalysts with nitrate precursors. The sintering of platinum in the catalysts of the C series was also indirectly confirmed by reoxidation of the metallic phase after TPR. Whereas pure platinum–alumina was quite easily reoxidized to Pt^{2+} (air treatment at 773 K), the reoxidation of platinum in the catalysts of the C series was very limited (35–40% of the theoretical value), in agreement with the formation of much larger platinum particles [12,13]. Furthermore, in the *n*-heptane conversion it was shown that the catalysts of the C-series presented high hydrogenolysis selectivity [14].

Finally, due to the recovery of both the extended metallic area and the catalytic activity after the destruction of nitrate species, it appears that lithium by itself has little effect on the intrinsic dehydrogenation properties of platinum.

4. Conclusions

Pt/Al_2O_3 catalysts modified by the addition of lithium nitrate are quite affected by the presence of residual nitrate species and are less sensitive to the presence of lithium, at least when considering the hydrogen adsorption properties and the behaviour in cyclohexane dehydrogenation.

The catalysts prepared by sequential impregnation with atomic ratio of Li/Pt between 3.5 and 4.7, led to a slightly better platinum dispersion when compared to the coimpregnated catalysts.

When the Li/Pt atomic ratio is close to 28, it is necessary to remove residual nitrate species, by increasing the final temperature of calcination of Li/Al_2O_3 in the absence of platinum precursor, to obtain satisfactory platinum dispersion.

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