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Characteristics of the metallic phase of Pt/Al_2O_3 and Na-doped Pt/Al_2O_3 catalysts for light paraffins dehydrogenation

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Abstract

The influence of the Na addition to Pt/Al_2O_3 catalysts is analyzed in this paper, not only on the characteristics and properties of both the acid and metallic function, but on the activity, selectivity and deactivation in the *n*-butane dehydrogenation reaction.

The addition of increasing amounts of Na to Pt/Al_2O_3 catalyst modifies both the nature of the acid function (by poisoning the stronger acid sites) and the metallic phase (by a geometric modification the metallic phase). These modifications would be the responsible for the sharp diminution of deactivation of the catalysts due to the carbon deposition. Na addition to Pt/Al_2O_3 catalysts inhibits the formation of coke deposited on the metallic sites and the support.

Keywords: Pt/alumina catalysts; Na-doped alumina; Butane dehydrogenation

1. Introduction

Pt-based catalysts supported on alumina are active for naphtha reforming and for dehydrogenation of low and high molecular weight paraffins [1–3]. One important difference between naphtha reforming and dehydrogenation catalysts is related to its acid character. Thus, a given acidity level in the reforming of hydrocarbon is required to obtain an adequate balance between the metallic function and the acid function in order to reach the bifunctional character [4]. In the case of the dehydrogenation catalysts, side reactions (cracking, isomerization and polymerization), which are catalyzed by acid centers, must be inhibited in order to increase the yield of the corresponding olefins. One way to minimize the undesirable side reactions is to poison the acid sites of the support by the addition of alkali metal ions during the preparation of the catalysts. It must be indicated that several studies on this topic have been reported in the literature. Thus, Pines and Haag [5] found that alkali metal ions poison the Lewis acid sites of the alumina. Jiratová and Beranek [6] reported a selective poisoning of the support when alumina is doped with Na ions. García Cortéz et al. [7], by using ammonia thermodesorption, found that Li, Na and K ions poison the acid sites of alumina. Moreover, these authors reported that the strong acid sites are poisoned by the addition of small quantities of alkali metal ions. Further addition of these ions blocks centers with lower acid strength. In addition, they also found that the toxicity of the alkali metals on the acid character of alumina increases with the ionic radius, though the poisoning effect of Na, K and Li would not be related only to a steric effect. Besides, de Miguel et al. [8] found, through FT-IR of pre-adsorbed CO and NMR measurements, that K and Li addition poisons mainly the OH configuration of type Ia (OH group bonded to tetrahedral Al^{3+}, according to the model of the alumina surface proposed by Knözinger and Ratnasamy [9]), this effect being more pronounced for K. However, the addition of alkali metals to alumina not only modifies the acid function, but also could affect the structure of the metallic phase. In fact, Mross [10] reported that the alkali metals could change the electronic structure of the transition metals, and in consequence the activity in the CO hydrogenation reaction would be enhanced. Park and Price [11,12] reported that the K addition to Pd/Al_2O_3 catalyst increases both the activity and the selectivity in the acetylene

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hydrogenation. This behaviour was explained in terms of the increase in the basicity of the support, followed by an electronic transference from K to Pd.

Besides, Martin and coworkers [13,14] studied alkali-promoted Ni/SiO_2 catalysts for alcohol synthesis and discussed the deactivation of alkali promoted catalysts in terms of the stabilization of Ni subcarbonyl species by alkali promoters. The stability of these systems varies according to the sequence: K > Na > Li > unpromoted.

In this paper, the influence of the Na addition to Pt/Al_2O_3 on the activity, selectivity and deactivation (by coke formation) in the *n*-butane dehydrogenation reaction is analyzed. Besides, a more detailed study of the effect of the alkali metal addition to Pt/Al_2O_3 catalysts on the characteristics and properties of both the acid and metallic function is reported.

2. Experimental

Catalysts were prepared by using a commercial γ-Al_2O_3 (CK 300 from Cyanamid Ketjen) previously calcined in flowing air at 923 K during 3 h. The alumina samples doped with Na in different concentrations (0.05, 0.15 and 0.25 wt.%) were obtained by impregnating the support with aqueous solution of NaOH. Pt (0.3%)/Al_2O_3–Na catalysts with different Na contents were prepared by successive impregnation: first Pt was deposited from an aqueous solution of H_2PtCl_6 (0.011 M). The impregnation volume/support weight ratio was 1.4 ml/g. After the impregnation, samples were dried at 393 K. Then Na was deposited through an impregnation with aqueous NaOH solutions (impregnation volume/catalyst weight ratio: 1.4 ml/g). The Na content in these samples ranged between 0 and 2 wt.%. Then, samples were dried at 393 K and finally calcined at 773 K in a flowing air during 3 h. Moreover, Pt (0.3 wt.%)/Al_2O_3 catalyst was prepared by alumina impregnation with an aqueous solution of H_2PtCl_6.

The acid properties of pure and Na-doped alumina samples were determined by isopropanol (IPA) dehydration reaction at 523 K and atmospheric pressure in a flow reactor, using a H_2/IPA molar ratio equal to 18 and a space rate of $32\,h^{-1}$.

Supported metallic catalysts were characterized by temperature programmed reduction (TPR) using a reducing mixture composed by H_2 (5%, v/v)–N_2 with a flow rate of 10 ml/min and a heating rate of $6\,K\,min^{-1}$ from room temperature up to 900 K.

The metallic dispersion was determined by H_2 chemisorption and the state of the metallic phase was also studied by using test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis). The H_2 chemisorption measurements were carried out at 298 K in a volumetric equipment. The catalyst was previously reduced with H_2 at 773 K during 3 h, and then it was outgassed under high vacuum (10^{-4} Torr) at the same temperature for 1 h. When the sample was cooled down to room temperature, the chemisorption test began. Test reactions of the metallic phase were performed in a differential flow reactor at atmospheric pressure. Cyclohexane (CH) dehydrogenation was carried out at 573 K, by using a H_2/CH molar ratio of 29 and a CH flow rate of $6\,ml\,h^{-1}$. Previous to the reaction catalysts were reduced at 573 or 773 K. The activation energy in CH dehydrogenation for different catalysts was obtained by measuring the initial reaction rate at 543, 558 and 573 K. The reaction conditions for cyclopentane (CP) hydrogenolysis were: temperature = 573 K, H_2/CP molar ratio = 25 and a volumetric flow of CP = $6\,ml\,h^{-1}$. Previous to the CP reaction, catalysts were reduced at 573 K. The sample weight used in these experiments was the appropriate to obtain a CH or CP conversion lower than 7%. The reaction products were only benzene and *n*-pentane for the first and second reaction, respectively. In both cases, the reaction products were analyzed by using a gas chromatographic system (packed column with Chromosorb and FID as detector).

The different catalysts (Pt/Al_2O_3 and Pt/Al_2O_3–Na) were tested in the *n*-butane dehydrogenation in a continuous flow reactor. Previous to the reaction, the different samples were reduced under H_2 flow at 803 K during 3 h. Then the reactor was fed with the reactive mixture composed by H_2 and *n*-butane (H_2 flow = $10\,ml\,min^{-1}$, *n*-butane flow = $8\,ml\,min^{-1}$). The sample weight was 0.2 g and the reaction temperature was 803 K in all cases. The first sample of the reactor effluent was taken after 10 min from the reaction beginning. Samples of the reaction products were analyzed in a GC system (packed column with 20% BMEA on Chromosorb PAW 60/80 and a FID as a detector). The total reaction time was 120 min. After the reaction, the used catalysts were characterized by temperature programmed oxidation (TPO) by using a O_2 (10 vol.%)/N_2 mixture and a heating rate of $10\,K\,min^{-1}$ in order to determine the coke content. TPO experiments were carried out in a differential flow reactor coupled to a mass spectrometer VG Quadrupoles for the analysis of the desorbed gases. Moreover, catalysts were tested in *n*-butane dehydrogenation reaction in a pulse equipment. This technique was used to obtain information about: (1) the catalytic behaviour in the first steps of the reaction, (2) the initial deposition of coke and (3) the effect of the coke deposition on the activity and selectivity. The pulse experiments were carried out at 803 K by injecting successive pulses of pure *n*-butane (pulse volume = $0.50\,cm^3$ STP) to the catalytic bed, which was maintained under He flow ($30\,ml\,min^{-1}$) between two successive pulses. Catalyst samples were previously reduced under flowing H_2 at 803 K, during 3 h. Reaction products were analyzed by a GC system (packed column with Porapak Q and FID as detector). The carbon amount deposited on the catalyst samples was determined by using a carbon mass balance in each pulse.

3. Results and discussion

3.1. Characterization of the acid and metallic phase

The poisoning effect of the alkali metals on the acid properties of the alumina was studied by means of the isopropanol (IPA) dehydration to propylene (P) and di-isopropylether (D). Fig. 1 shows that the isopropanol conversion decreases as the amount of Na increases. It can also be observed that very low amounts of Na (0.25 wt.%) added to Al_2O_3 produce an almost total inhibition of the dehydration capacity. Moreover, the selectivity to di-isopropylether displays an analogous behaviour since it decreases with the increase of the Na content, such as Fig. 1

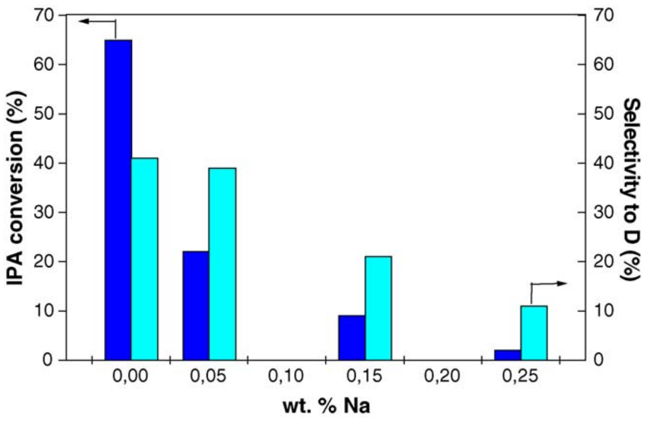

Fig. 1. Total isopropanol (IPA) conversion and selectivity to di-isopropylether (D) (conversion to di-isopropylether × 100/conversion to propylene) as a function of the Na content added to alumina.

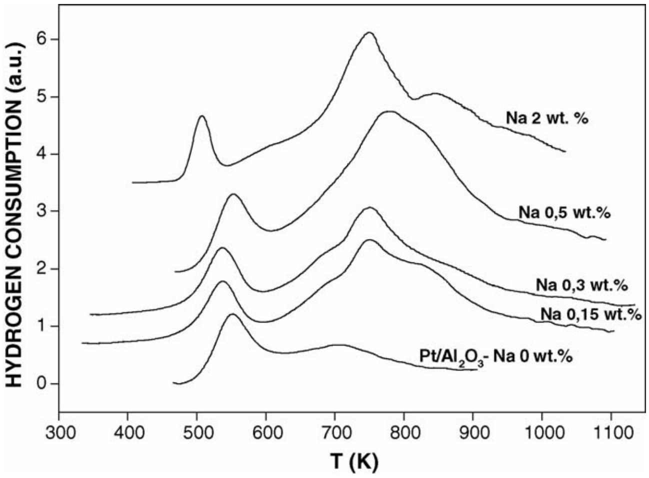

Fig. 2. Temperature programmed reduction (TPR) profiles of calcined Pt/Al_2O_3 and Pt/Al_2O_3–Na (0.15–2 wt.%) catalysts.

also shows. Taking into account that the ether formation would require strong acid sites [7], the results obtained in the isopropanol dehydration would be in agreement with the higher poisoning capacity of Na on the stronger acid sites of the alumina.

Fig. 2 shows TPR profiles of Pt/Al_2O_3 and Pt/Al_2O_3–Na catalysts (with different Na contents). The profile of the undoped monometallic catalyst shows two peaks: a main one at about 540 K and a second smaller one at about 690 K. It can be observed that the first reduction peak in the Pt/Al_2O_3–Na (2 wt.%) catalyst appears at 500 K and it is clearly shifted to a lower temperature with respect to the corresponding to the monometallic one. This effect could be due both to an increase of the metal particle size and a modification of the Pt–support interaction by the Na addition. It must be also noted that the second reduction peak is shifted to higher temperatures in Pt/Al_2O_3–Na catalysts (with a maximum at approximately 715 K) with respect to that of Pt/Al_2O_3 catalyst, and its intensity also increases as the Na content increases. This behaviour could be attributed to the formation of new species with lower reducibility in Pt/Al_2O_3–Na catalysts with respect to the undoped monometallic one, or to a higher interaction of these species with the support. The concentration of these new species appears to increase for higher Na contents in the catalyst. Besides, this effect is followed by a diminution of the concentration of the Pt species corresponding to the first TPR peak. These results indicate that the addition of increasing amounts of Na leads to a modification of the metallic phase.

Table 1 shows the metallic dispersion values obtained by H_2 chemisorption, the initial reaction rate (R_{CH}) and the activation energy (E_{CH}) values in CH dehydrogenation reaction, and the initial reaction rate values in cyclopentane hydrogenolysis (R_{CP}), for catalysts with different Na contents. Table 1 also shows that the metallic dispersion values decrease when the Na content increases. The results on the CH dehydrogenation indicate that the initial reaction rate decreases when increasing Na amounts are added to Pt/Al_2O_3 catalyst. It must be also noted that the activation energy (E_{CH}) values in this reaction are similar for all the catalysts. These results could indicate that the decrease of both the metallic dispersion and the dehydrogenation activity in doped catalysts would be related to a geometric modification of the Pt particles.

An important decrease of the hydrogenolytic activity with an increasing Na content is observed in Table 1. Taking into account the sensitive-structure character of this reaction, the CH dehydrogenation results and the H_2 chemisorption measurements, it can be inferred that the Na addition would cause only a geometric modification of the metallic phase, thus, producing blocking and dilution effects. In all cases the increasing amounts of Na added to Pt would produce a parallel diminution of the concentration of Pt ensembles necessary to catalyze the CP hydrogenolysis.

Table 1
Values of metallic dispersion (D), initial rates (R_{CH}) and activation energy (E_{act}) for cyclohexane (CH) dehydrogenation and initial rates (R_{CP}) for cyclopentane (CP) hydrogenolisis, for catalysts of Pt (0.3%)/Al_2O_3–Na (with different Na contents)

% Na	D (%)	CP hydrogenolysis	CH dehydrogenation reduction at 573 K		CH dehydrogenation reduction at 773 K	
		R_{CP} (mol/h g Pt)	R_{CH} (mol/h g Pt)	$E_{act.}$ (Kcal/mol)	R_{CH} (mol/h g Pt)	$E_{act.}$ (Kcal/mol)
0	86	2.4	108	23	102	23
0.3		1.3	96	22	93	23
0.5	70	1.2	68	24	82	23
1	61	0.4	40	24	46	22
2		0	18	29	19	26

Table 2
Values of initial conversion obtained at 10 min of reaction (X_0), deactivation parameter defined as [$(X_0 - X_f)/X_0 \times 100$]; X_f is the final conversion, initial selectivity (S_0) and final selectivity (S_f) to butanes, and initial $[S_{1\text{-B}}/S_{2\text{-B}}]_0$ and final $[S_{1\text{-B}}/S_{2\text{-B}}]_f$ ratios between 1-butene and 2-butenes (*cis*-2-butene + *trans*-2-butene)

Catalyst	X_0 (%)	$(X_0 - X_f)/X_0$ (%)	S_0 (%)	S_f (%)	Initial ($S_{1\text{-B}}/S_{2\text{-B}}$)	Final ($S_{1\text{-B}}/S_{2\text{-B}}$)
Pt/Al_2O_3	44.5	78	53	50	0.85	0.67
Pt/Al_2O_3–Na (0.3%)	36.5	64	74	69	0.49	0.43
Pt/Al_2O_3–Na (0.5%)	25.8	49	77	77	0.46	0.47
Pt/Al_2O_3–Na (1%)	25.7	49	73	70	0.51	0.53
Pt/Al_2O_3–Na (2%)	8.2	48	80	76	0.53	0.61

Reaction temperature: 803 K.

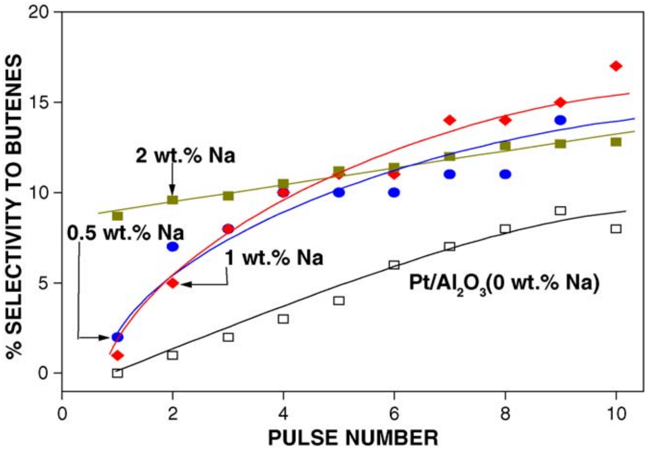

Fig. 4. Selectivity to butenes (S) as a function of the number of pulses for the Pt/Al_2O_3 and Pt/Al_2O_3–Na (0.5–2 wt.%) catalysts.

3.2. Catalytic test in *n*-butane dehydrogenation

It must be indicated that the main products obtained in the catalytic tests were: (paraffins and olefins) < C_4 (derived from hydrogenolysis and cracking reactions), 1-butene, *cis*- and *trans*-2-butenes and, in a minor proportion, butadiene. Table 2 shows the catalytic results [initial *n*-butane conversion, X_0; deactivation parameter defined as: $100 \times (X_0 - X_f)/X_0$, where X_f is the final conversion; initial (S_0) and final (S_f) selectivities to butenes (1-butene + *cis*-2-butene + *trans*-2-butene + butadiene) of the different catalysts in the *n*-butane dehydrogenation reaction at 803 K in a continuous flow reactor. Results show that when the Na content added to Pt/Al_2O_3 catalyst increases, different effects are observed: (1) the initial conversion decreases, (2) the deactivation parameter also decreases, and (3) the selectivity (both initial and final) tends to increase.

The lower deactivation capacity of Pt/Al_2O_3–Na catalysts, with respect to the undoped sample, could be attributed to the presence of the alkali metal in the vicinity of the noble metal with the subsequent diminution of coke deposited on the metallic phase. In order to verify the validity of this assumption, additional experiments of *n*-butane dehydrogenation were carried out in a pulse system. Results obtained in a pulse system are shown in Figs. 3–5, which displays the *n*-butane conversion, the selectivity to butenes and the relative carbon retention in the catalyst, as a function of the number of pulses. The *n*-butane conversion (Fig. 3) was very high for the first pulses of butane injected to the undoped Pt/Al_2O_3 catalyst, and it decreased as the Na content in the catalyst increased. For the Pt/Al_2O_3–Na (2 wt.%), the conversion was low and almost constant along the successive pulses. The selectivity to butenes (Fig. 4) increased with the pulse number and it was higher for the Na-doped catalysts.

The relative carbon retention (Fig. 5) was very high for the undoped Pt/Al_2O_3 catalyst and it decreased as the Na content in the catalyst increased. It must be indicated that the relative reten-

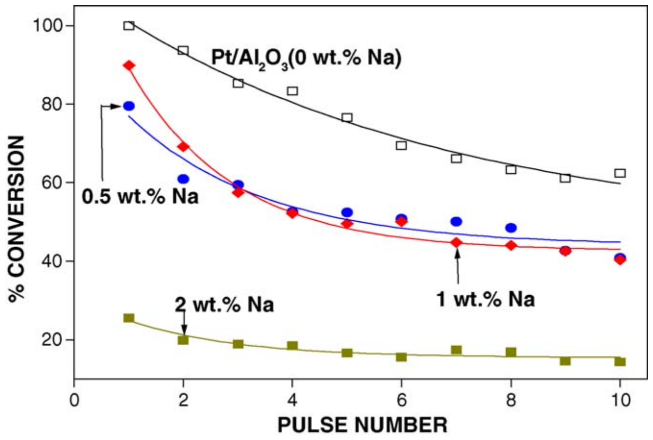

Fig. 3. Butane conversion as a function of the number of pulses for the Pt/Al_2O_3 and Pt/Al_2O_3–Na (0.5–2 wt.%) catalysts.

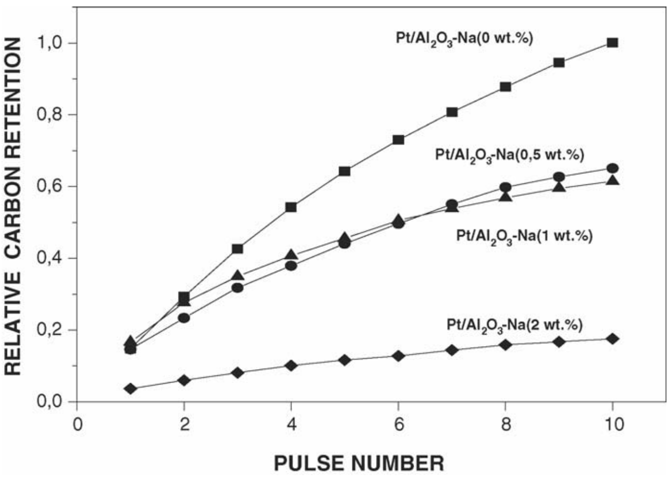

Fig. 5. Relative carbon retention as a function of the number of pulses for the Pt/Al_2O_3 and Pt/Al_2O_3–Na (0.5–2 wt.%) catalysts.

tion of carbon represents the cumulative amount of deposited coke on catalysts after each pulse and respect to the amount of coke deposited on the Pt/Al_2O_3 catalyst after 10 pulses of *n*-butane injected to the reactor. Fig. 5 shows a very important carbon retention in the undoped Pt/Al_2O_3 catalyst, mainly in the first pulses, this effect being less pronounced in the catalysts with Na contents of 0.5 and 1 wt.%. At higher Na contents (2 wt.%), the carbon retention is very low, but it must be taken into account that the butane conversion is also low in this catalyst.

The deactivation parameters observed in the flow experiments between the different catalysts (without and with Na) decrease from 78% for the undoped sample to 48% for the Pt/Al_2O_3–Na (2%) one. However, the differences of carbon retention between the undoped and doped catalysts (observed in the pulse experiments) are very important, such as it can be seen in Fig. 5. Hence, the main carbon deposition (and deactivation) is produced during the initial stage of the reaction. In the case of the flow system, the first sample of reaction products was taken at 10 min from the beginning of the reaction, and it would correspond to a catalytic surface with an important amount of deposited carbon. In consequence, the avoidance of the coke deposition is shown more clearly in pulse experiments than in flow ones.

The conversion of *n*-butane is very high after injection of the first pulses to a Pt/Al_2O_3 sample, but the selectivity to butenes is very low (this means that the selectivity to hydrogenolysis is very high). Similar results were obtained during the initial stages of propane dehydrogenation using a similar monometallic catalyst [15]. As the number of pulses increases, the conversion (Fig. 3) and the percentage of carbon retained in each pulse (Fig. 5) decrease with respect to the previous pulse and the hydrogenolysis quickly decreases leading to an increment in the selectivity to butenes (Fig. 4). Results introduced in Figs. 3–5 indicate that at the beginning of the reaction (first pulses) for Pt/Al_2O_3 catalyst, the hydrogenolysis and cracking are the main reaction routes. In this case the metallic phase shows very high activity, but it is quickly poisoned by coke with the consequent catalyst deactivation. After the injection of several pulses, the hydrogenolytic activity decreases and the selectivity to butenes increases. Comparing the Pt/Al_2O_3 sample with the Pt/Al_2O_3–Na ones in pulse experiments, the following trend in stability (related to deactivation and carbon retention) of the catalyst with the increase of Na content in the catalyst was observed (see Figs. 3 and 5):

$$\mathrm{Pt/Al_2O_3\text{–}Na\,(2\,wt.\%)} > \mathrm{Pt/Al_2O_3\text{–}Na\,(1\,wt.\%)}$$
$$> \mathrm{Pt/Al_2O_3\text{–}Na\,(0.5\,wt.\%)} > \mathrm{Pt/Al_2O_3}$$

Similar results were obtained for catalysts supported on K-doped Al_2O_3 in propane dehydrogenation [16]. In this paper, the authors reported that K addition to Pt/Al_2O_3 and $PtSn/Al_2O_3$ catalysts significantly decreases the catalyst deactivation by lowering the amount of coke deposited on the support and metal, and producing coke with a lower polymerization degree.

Catalysts tested in *n*-butane dehydrogenation during 2 h at 803 K, were characterized by temperature programmed oxidation (TPO) experiments, and their profiles are shown in Fig. 6. The TPO profile of Pt/Al_2O_3 catalyst shows two peaks: the former, appearing at lower temperatures, would correspond to coke placed near to the metallic surface, and the latter at higher temperatures, would be due to the carbon deposited on the support [17]. The second peak that corresponds to the coke deposited on alumina, is clearly decreased in the Na-doped catalysts, where the acid sites were poisoned by the alkali metal addition. A decrease of the coke deposited on the metal (first peak) as the Na concentration in the catalysts increased, is also observed in Fig. 6.

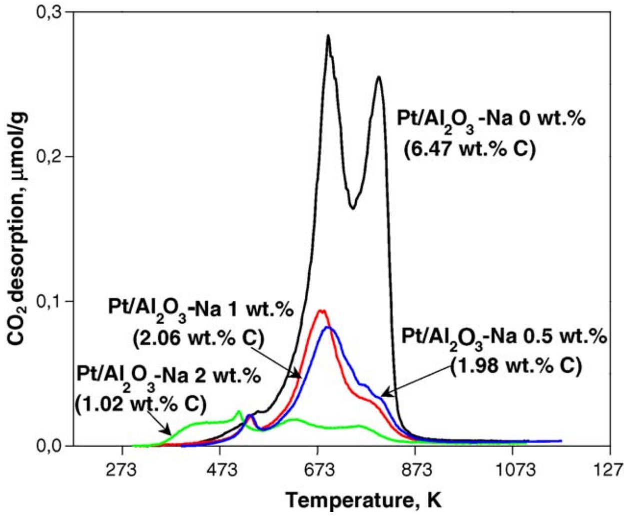

Fig. 6. Temperature programmed oxidation (TPO) profiles of the different catalysts. Carbon contents (obtained from the TPO results) are shown between brackets.

The formation of carbon deposits on the catalyst, with the consequent catalyst deactivation, is produced by the polymerization of the olefins formed during the dehydrogenation. The polymerization reaction is catalyzed both by acid and metallic sites. In the last case (catalysis by the metallic function) the reaction behaves as a demanding one and it is carried out on the same type of sites as the hydrogenolysis, thus, requiring determined ensembles of Pt atoms. From our results, it has been shown that the Na on Pt/Al_2O_3 catalysts not only poisons the acid sites of the alumina but also produces a geometric modification of Pt sites as well, thus, decreasing the hydrogenolytic ensembles responsible for the coke deposition. These important modifications in the catalyst structure by the Na addition would cause the pronounced diminution of the deactivation by the carbon deposition.

Finally, Table 2 also shows the initial and final ratios between the selectivity to 1-butene and 2-butenes (*cis*-2-butene + *trans*-2-butene) [$S_{1\text{-B}}/S_{2\text{-B}}$]. Results indicate that there is a certain modification in $S_{1\text{-B}}/S_{2\text{-B}}$ ratio when the Pt/Al_2O_3 catalyst is doped with increasing Na concentrations. The modification of the $S_{1\text{-B}}/S_{2\text{-B}}$ ratio was also observed in the pulse experiments, which give information about the first stage of the reaction, such as it was observed in Fig. 7. From the results obtained in both flow and pulse experiments, we can say that the isomerization of 1-butene to *cis*- and *trans*-2-butenes would be slightly higher for Na-doped catalysts than on undoped samples. In these doped catalysts, the isomerization would be mainly carried out only on

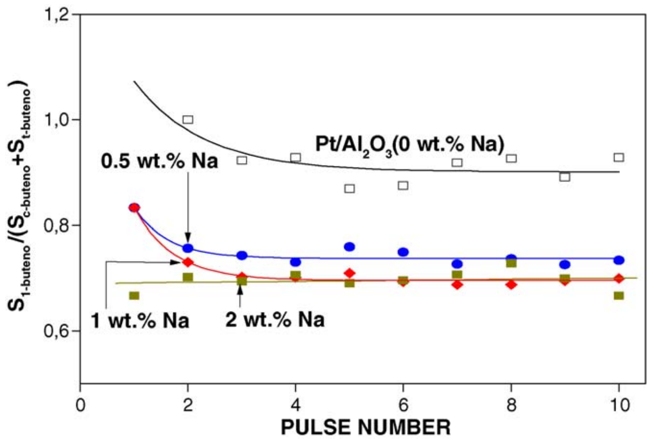

Fig. 7. Ratio between the selectivity to 1-butene and that to 2-butenes (*cis*-2-butene + *trans*-2-butene) [$S_{1\text{-B}}/S_{2\text{-B}}$] as a function of the number of pulses for the Pt/Al_2O_3 and Pt/Al_2O_3–Na (0.5–2 wt.%) catalysts.

metallic sites because of the poisoning of the acid sites by the presence of the alkali metal [5–8].

4. Conclusions

1. Results obtained in the isopropanol dehydration reaction would indicate the poisoning effect of Na on the stronger acid sites of the alumina.
2. The addition of increasing amounts of Na to Pt/Al_2O_3 catalyst leads to a geometric modification of the metallic phase.
3. These modifications in the catalyst structure by the effect of Na addition would cause the pronounced diminution of the ensembles for hydrogenolysis and carbon formation, thus, producing catalysts with a lower deactivation by coke deposition.
4. Two different types of coke are deposited on the alumina: a fraction deposited near to the metallic surface, and another one adsorbed on the support. Na addition to Pt/Al_2O_3 catalysts inhibits the formation of both types of coke, mainly that originated on the acid sites of the alumina, which are poisoned by the alkali metal.
5. There is a modification in the ratio between the selectivity to 1-butene and that of 2-butenes when Pt/Al_2O_3 is doped with increasing Na concentrations.

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