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Characterization and dehydrogenation activity of Pt/Nb_2O_5 catalysts

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Abstract

Pt/Nb_2O_5 catalysts were prepared with different loadings of Pt and characterized by TPR, DRS, H_2 and CO chemisorption and H_2/O_2 titration. Higher metal content catalysts presented an increasing SMSI effect related to a lower adsorption capacity. The Pt blocking by NbO_x species causes the formation of new interfacial active sites. After a high temperature reduction, the catalysts were highly selective towards dehydrogenation products and total inactive for hydrogenolysis in the case of n-heptane conversion.

Keywords: Pt/Nb_2O_5 catalysts; Dehydrogenation activity

1. Introduction

Dehydrogenation of long chain paraffins is usually performed with alumina supported bimetallic catalysts, such as $Pt–Sn/Al_2O_3$ [1,2]. Recently, an alternative Pt/Nb_2O_5 catalyst has been studied in hydrocarbon conversions [3,4]. The initial results for n-heptane dehydrogenation on this catalyst displayed a higher selectivity towards the formation of olefins as compared to the ones obtained with conventional catalysts. Besides, the formation of aromatics and light products was minimized. These effects have been associated to the low acidity of calcined niobia and to an ensemble effect promoted by niobia reduced species of the platinum surface (strong metal support interaction, SMSI). Even though a great number of studies have dealt with Pt/TiO_2 catalysts [5–7], the metallic surface characterization of Pt/Nb_2O_5 has not received much attention. Therefore, it seemed of interest to further characterize the metallic surface of Pt/Nb_2O_5 catalysts and correlate the results with the catalytic properties.

In this work, the influence of platinum content on the structure of metallic particles, degree of SMSI and catalytic properties of Pt/Nb_2O_5 was investigated. These systems were characterized by temperature-programmed reduction (TPR), hydrogen and carbon monoxide chemisorption and UV–Vis spectroscopy. Catalytic activity and selectivity were evaluated by cyclohexane and n-heptane dehydrogenation.

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2. Experimental

2.1. Catalyst preparation

The Nb_2O_5 support (BET area = 65 m^2/g) was obtained by calcination of niobic acid (CBMM, HY 340/AD 929) in air at 773 K for 2 h. The Pt/Nb_2O_5 catalysts were prepared by incipient wetness technique using an aqueous solution of H_2PtCl_6 (Reagen), followed by drying at 393 K for 16 h and calcination in air at 773 K for 2 h. The platinum loadings were 0.5, 0.8, 1.0 and 2.0 wt.-%.

2.2. TPR

The TPR apparatus and methodology of analysis have been described previously [8]. The precursors were dehydrated at 393 K, under flowing Ar before the reduction. A gaseous mixture of 1.5% hydrogen in argon was passed through the sample and the temperature was raised to 573 or 773 K at a heating rate of 10 K/min.

2.3. Diffuse reflectance UV–Vis spectroscopy

The samples were characterized at room temperature in a VARIAN model Cary 5 UV–Vis–NIR spectrophotometer equipped with a Diffuse Reflectance Accessory (HARRICK). In order to separate the contribution from the support, the reflectance $r(\lambda)$ of the sample was ratioed to the reflectance of the support and the Kubelka–Munk function was calculated.

2.4. Chemisorption measurements

Irreversible hydrogen chemisorption and H_2/O_2 titration were performed at the same apparatus of the TPR. After purging the sample with an Ar gas flow at the reduction temperature for 30 min, the irreversible amount of adsorbed H_2 was measured by the frontal method [9]. The H_2/O_2 titration was carried out by exposing the samples to a 21% O_2/N_2 stream, purging with Ar, and repeating the procedure of hydrogen chemisorption for the titration of adsorbed oxygen at the surface.

Carbon monoxide uptakes were measured by the static volumetric method, in an automatic adsorption system (ASAP 2900, Micromeritics). Adsorption isotherms were obtained at 60–200 mm Hg pressure range and 298 K. Reversible adsorption isotherms were obtained after evacuating the samples at 10^{-6} Torr for 30 min. Hydrogen uptake and H_2/O_2 titration were also obtained by the static volumetric method for some samples at similar conditions.

2.5. Catalytic activity

The vapor-phase cyclohexane dehydrogenation experiments were performed in an atmospheric glass microreactor. The reactant mixture (H_2/cyclohexane = 13) was obtained by contacting H_2 and cyclohexane in a saturator kept at 285 K. The pretreatment of the samples consisted of drying at 393 K for 30 min under flowing N_2, followed by reduction in 5% H_2/N_2 at 773 K for 30 min. Then each catalyst was cooled to the reaction temperature (543 K) under the reducing gaseous mixture. The reactor effluent was analyzed using an on-line gas chromatograph equipped with a flame ionization detector and a 4.5 m Carbowax 20 M on Chromosorb packed column.

The dehydrogenation of n-heptane was also carried out in a atmospheric glass microreactor. The samples were pretreated as described in the case of cyclohexane dehydrogenation. The reactant mixture was obtained in a saturator kept at 298 K, which led to an H_2/n-heptane ratio equal to 16. The reaction temperature was 773 K and the products were analyzed using a gas chromatograph equipped with a flame ionization detector and a 50 m $KCl–Al_2O_3$ capillary column.

For both catalytic reactions, conversions were kept below 10%, so that the reactors could be considered as a differential one and the selectivities were compared at the same conversion.

3. Results and discussion

Fig. 1 shows the TPR profiles of the catalysts studied. All the sample profiles displayed a peak in the range of 343–363 K, which can be assigned to the reduction of superficial platinum oxide, α-PtO_2 [10]. Besides, the samples of higher platinum content (0.8, 1.0%) showed some room temperature reduction, which is characteristic of the reduction of bulk PtO_2, with low interaction with the support.

The profile of the 0.5% Pt/Nb_2O_5 catalyst displayed an additional peak at 407 K. This peak is tentatively ascribed to the presence of a oxychloroplatinum superficial complex. In the case of Pt/Al_2O_3 catalysts, the oxychloroplatinum complex reduces in the range of 480–560 K [10]. This species would be formed during drying and calcination, due to the residual chloride ions on the support.

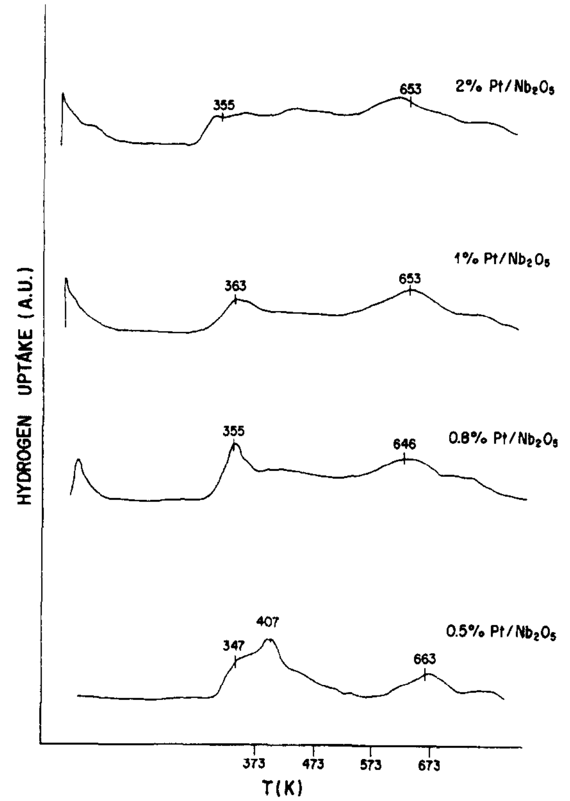

Fig. 1. TPR profiles of Pt/Nb_2O_5 catalysts.

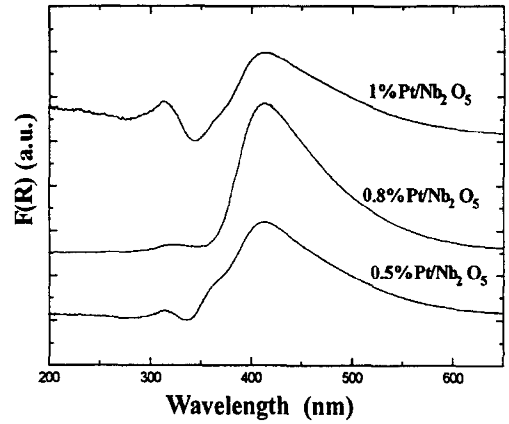

Fig. 2. DRS spectra of calcined Pt/Nb_2O_5 catalysts.

The reduction of the Nb_2O_5 support was observed for all the samples, with a maximum of reduction around 643–663 K. The reduced species (NbO_x) are probably responsible for the changes in catalytic and chemisorptive properties of the catalysts after reduction at high temperatures [3,4,11,12].

The results obtained with UV–vis diffuse reflectance spectroscopy were very consistent with the findings obtained by TPR. The spectra of the calcined samples are shown in Fig. 2. A main band with a maximum at 415 nm was observed for all the samples. This band indicates the presence of $PtO_2 \cdot H_2O$ [10]. A shoulder at 360 nm was also noted and it is ascribed to the presence of α-PtO_2. This result points to an equilibrium of the hydration of α-PtO_2, according to the reaction $\alpha\text{-}PtO_2 + H_2O \leftrightarrow PtO_2 \cdot H_2O$, due to the exposition of the samples to air.

Furthermore, a small band at 312 nm was observed for all the catalysts. Lieske et al. [10] have reported UV–vis spectra of supported metallic platinum with a band at this wavelength. Metallic platinum could be formed by decomposition of PtO_2 during the calcination step. Another possibility for the presence of this band is a charge transfer from the oxide ligands to platinum.

The spectra of 0.8% and 0.5% Pt/Nb_2O_5 catalysts recorded after reduction and passiva-

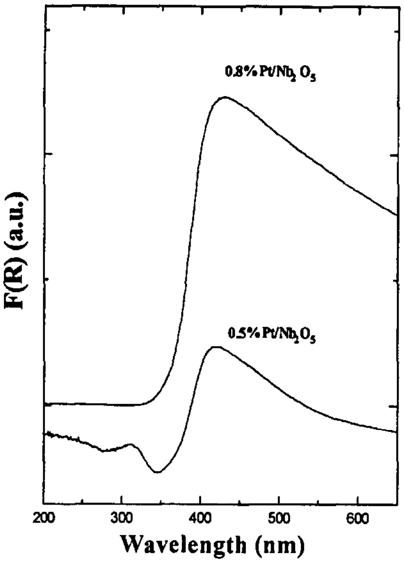

Fig. 3. DRS spectra of Pt/Nb_2O_5 catalysts reduced and passivated.

tion are shown in Fig. 3. Besides the band at 412 nm in the d–d transition range, a band in the charge transfer range is observed at 277 nm for the 0.5% Pt/Nb_2O_5. In the case of Pt/SiO_2 catalysts, this band has been ascribed to the charge transfer from chlorine to platinum by Lopez et al. [13], while for Pt/Al_2O_3 catalysts this band was related to the presence of oxychloroplatinum complex. These results agree with the TPR profile of 0.5% Pt/Nb_2O_5, which indicated the presence of oxychloroplatinum complex in these samples.

Hydrogen, H_2/O_2 titration and carbon monoxide uptakes are listed in Table 1. After a low reduction temperature, most of the catalysts presented similar H/Pt values, around 0.3. A lower value (0.15) was obtained for the 2.0% Pt/Nb_2O_5 catalyst. After the high temperature reduction, there was a decrease in H_2 uptake for all the samples and the extent of this decrease seems to be greater for the catalysts with higher Pt loading.

For most of the samples, after calcination and low temperature reduction, the $(H/Pt)_T$ values calculated from the results of H_2/O_2 titration are very similar to the H/Pt values obtained by H_2 chemisorption. The H_2/O_2 titration values for the samples reduced at 773 K, are much higher than the values obtained by H_2 adsorption. These results can be interpreted in terms of the migration and bonding of a niobium suboxide on the platinum particles. This phenomenon is usually called SMSI [14,15]. In this case, the chemisorption capacity is fully restored after an oxidation treatment, showing that the SMSI effect is broken in an easier way in the case of Pt/Nb_2O_5 catalysts than for $metal/TiO_2$ catalysts, for which oxidation at higher temperatures is necessary to fully restore the chemisorption capacity [16]. Similar behavior was observed for $Pt/Nb_2O_5–Al_2O_3$ [17] and Ir/Nb_2O_5 catalysts [18].

The H_2/O_2 titration results for 2% Pt/Nb_2O_5

Table 1
H_2, H_2/O_2 titration and CO uptakes on Pt/Nb_2O_5 at 298 K

Catalyst	H_2 uptake (μmol/g cat.)	H/Pt	H_2/O_2 titration (μmol/g cat.)	$(H/Pt)_T$	CO uptake [c] (μmol/g cat.)	CO/Pt
0.5% Pt/Nb_2O_5 (LTR) [a]	4.0	0.31	12.8	0.33	–	–
0.5% Pt/Nb_2O_5 (HTR) [b]	1.0 (1.0) [c]	0.08 (0.08) [c]	12.3	0.32	2.5	0.098
0.8% Pt/Nb_2O_5 (LTR) [a]	5.6	0.27	16.8	0.27	–	–
0.8% Pt/Nb_2O_5 (HTR) [b]	1.1	0.055	16.6	0.27	–	–
1.0% Pt/Nb_2O_5 (LTR) [a]	7.0	0.27	24.0	0.31	–	–
1.0% Pt/Nb_2O_5 (HTR) [b]	0.7 (1.3) [c]	0.027 (0.051) [c]	24.0	0.31	3.0	0.059
2.0% Pt/Nb_2O_5 (LTR) [a]	7.6	0.15	40.2	0.26	–	–
2.0% Pt/Nb_2O_5 (HTR) [b]	0.6 (2.4) [c]	0.012 (0.047) [c]	43.8	0.28	4.0	0.039

[a] After reduction at 573 K.
[b] After reduction at 773 K.
[c] Values obtained by the static method.

Table 2
Cyclohexane dehydrogenation on Pt/Nb_2O_5 catalysts after high temperature reduction

Catalyst	Initial rate [a]	TOF (s^{-1})
0.5% Pt/Nb_2O_5	10.8	3 (0.45) [b]
0.8% Pt/Nb_2O_5	48.3	6 (1.20) [b]
1.0% Pt/Nb_2O_5	50.4	10 (1.00) [b]
2.0% Pt/Nb_2O_5	51.8	12 (0.95) [b]

$T = 543$ K, $pH_2/pHC = 13$, $P = 1$ atm.

[a] Mol cyclohexane/(h g cat.) ($\times 10^3$).

[b] Turnover Frequency based on reaction rate after reduction at 773 K and hydrogen chemisorption after reduction at 573 K.

indicate that there is probably the occurrence of an SMSI, in a small extent, after the reduction at low temperature; in this case the $(H/Pt)_T$ values are higher than the H/Pt values obtained from hydrogen chemisorption results. Thus, the relative low value of H/Pt obtained for this catalyst after the low temperature reduction may not imply that the particle sizes of this catalyst are larger.

A comparison of the hydrogen uptakes obtained by the frontal method with those obtained by the static method shows that the results are in good agreement when the uptakes obtained by the frontal method are higher than 1.0 μmol/g cat. There is some discrepancy, however, for low values of H/Pt. Carbon monoxide is usually quite consistent with the hydrogen uptakes obtained by the volumetric method.

The activities of the several catalysts obtained for the cyclohexane dehydrogenation are listed in Table 2. There is some variation on the obtained turnover frequencies (TOF), based on the H/Pt values measured after reduction at 773 K. TOF values were usually higher for catalysts with higher Pt loading. Thus, we can observe that an increase in the SMSI intensity, measured by higher decrease in the chemisorption, promotes a larger number of interfacial active sites. The use of hydrogen uptake of a sample reduced at 773 K to evaluate the number of available sites is probably an underestimation, because there is the formation of interfacial sites upon support reduction. Therefore, for reducible oxides, common practice has been to report TOF based on percentage exposed measured on the same catalyst after a low temperature reduction [19,20]. The TOF values calculated, following this procedure, did not change for the several catalysts studied. This result is in agreement with the fact that reduction of metals supported on reducible oxides has only a minor effect on structure insensitive reactions [21].

As shown in Table 3, turnover frequencies for the n-heptane conversion on the several catalysts studied were similar and the trend was the same for TOF's calculated by either using hydrogen chemisorption uptakes after reduction at 773 or 573 K as an estimation of the number of sites.

A striking characteristic of the selectivity of products for the n-heptane conversion on Pt/Nb_2O_5 catalysts is the total suppression of hydrogenolysis products. A decrease in the rate of hydrogenolysis reactions has been previously described for niobia supported catalysis [4,22] and for TiO_2-supported catalysis [23,24]. This

Table 3
n-Heptane conversion on Pt/Nb_2O_5 catalysts after reduction at 773 K

Catalyst	TOF (s^{-1}) [a]	Selectivity (%)		
		Dehydrogenation	Aromatization	Isomerization
0.5% Pt/Nb_2O_5	0.12 (0.04) [b]	71	11	18
0.8% Pt/Nb_2O_5	0.21 (0.05) [b]	70	12	18
1.0% Pt/Nb_2O_5	0.30 (0.03) [b]	85	5	10

$T = 773$ K, $pH_2/pHC = 16$, $P = 1$ atm.

[a] Turnover frequency based on the reaction rate after reduction at 773 K and hydrogen chemisorption after reduction at 773 K.

[b] Turnover frequency based on the reaction rate after reduction at 773 K and hydrogen chemisorption after reduction at 573 K.

phenomenon is explained by a decrease on the size of platinum ensembles by the covering of platinum particles by reduced oxide species (TiO_x, NbO_x), in a similar way to the ensemble effect that is observed for bimetallic platinum catalysts [25,26].

Another interesting result, is the higher selectivity for the formation of olefins as compared to the formation of toluene and of isomerization products.

The acidity of Pt/Nb_2O_5 catalysts is rather low [4], which indicates the n-heptane conversion proceeds through a monofunctional pathway for these catalysts. Aromatics formation by a monofunctional mechanism proceeds by direct 1,6 or 1,5 ring closure after olefin formation [27–29]. Aromatization requires a larger ensemble than dehydrogenation [30], therefore, the higher selectivity to olefins observed in this study could be again explained by the geometric effect, i.e., the decoration of the metallic particles by the partially reduced support decreases the number of Pt atoms in an ensemble.

The selectivity towards olefin formation was higher for the catalysts with higher platinum content. This result is consistent with the chemisorption data, which indicated an increase of the interaction between metal and support with the increase of platinum content. The catalysts have similar particle sizes, as measured by hydrogen chemisorption after low temperature reduction. Thus, the catalysts of higher platinum loading possess higher metallic surface area, which could improve the dissociative adsorption of hydrogen and consequent spillover of atomic hydrogen [31] improving the reduction of the support.

4. Conclusion

The effect of high temperature reduction on the properties of Pt/Nb_2O_5 catalysts, with different Pt loadings, was investigated. TPR and diffuse reflectance UV-Vis spectroscopy results indicated that the main species on the surface after calcination of the precursors is α-PtO_2. The extent of Pt blocking by migration of a reduced species of the support is larger for the samples with a higher platinum content. This migration causes the formation of new interfacial sites that are active for dehydrogenation, but inactive for hydrogenolyis. The main mechanism for the suppression of hydrogenolysis and aromatization activity seems to be the dilution of metallic particles by niobium suboxide species according to the geometric model.

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