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Effect of preparation method on the properties of Nb_2O_5 promoted platinum catalysts

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Abstract

Pt/Nb_2O_5 catalysts were prepared on a reducible support by ion exchange and incipient wetness of different platinum salts. The $Pt/Nb_2O_5/Al_2O_3$ catalysts were prepared with several loading of niobium oxide over alumina, aiming different surface coverages and platinum dispersions. These catalysts were characterized by using different techniques: TPR, DRS, chemisorption of H_2, CO, CO_2 and pyridine. The catalytic activity was evaluated in the *n*-heptane conversion. Platinum oxide was the main surface precursor on the Nb_2O_5 supported catalysts, while a oxychloroplatinum surface complex was the precursor for $Pt/Nb_2O_5/Al_2O_3$ catalysts. These different precursors promote the formation of different platinum particle sizes, being the $Pt/Nb_2O_5/Al_2O_3$ samples more disperse. After high temperature of reduction, the platinum adsorption capacity decrease on all the samples, due to the reduction of Nb_2O_5, and subsequent blocking of surface platinum atoms. Nb_2O_5 and Nb_2O_5/Al_2O_3 supported catalysts are very selective to olefins in the *n*-heptane conversion. Furthermore, Brönsted acidic sites are formed on $Pt/Nb_2O_5/Al_2O_3$ catalysts with higher Nb_2O_5 loading, leading to a better stability of the catalysts.

Keywords: Pt supported catalysts; Dehydrogenation; Nb_2O_5; Nb_2O_5/Al_2O_3

1. Introduction

Dehydrogenation of paraffins has attracted increasing attention due to the high demand for the production of oxygenated compounds in reformulated gasoline and the long chain olefins to obtain biodegradable detergents [1,2]. These processes are usually performed with silica or alumina supported platinum catalysts modified by another metal such as tin or indium [3–5]. Despite of several studies related to the structure and the catalytic properties of this type of bimetallic systems, a definite model of relevance between the ligand and geometric effects is still controversial [6,7]. However, the dilution of platinum by the other metal over the support is a well-established point.

Recently, an alternative Pt/Nb_2O_5 catalyst has been studied in hydrocarbon conversions [8–10]. The initial results for *n*-heptane dehydrogenation on this catalyst displayed a higher selectivity towards the formation of

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olefins as compared to the conventional catalysts. Moreover, the formation of aromatics and light products were minimized. These effects have been associated to the low acidity of calcined niobia and to an enhanced ensemble effect promoted by niobia reduced species on the platinum surface (Strong Metal Support Interaction – SMSI).

In this work, the preparation method of Pt/Nb_2O_5 catalysts by incipient wetness and the ion exchange was investigated using different platinum precursors. The Pt/Nb interaction was also studied for $Pt/Nb_2O_5/Al_2O_3$ catalysts, aiming to follow the interaction effects on the selectivity towards olefins formation. The Nb content was varied until the monolayer was reached. Furthermore, the Nb_2O_5/Al_2O_3 catalysts were obtained by a new method of niobium oxalate impregnation on alumina. Wachs [11] used niobium oxalate for coating on alumina support and observed that the monolayer is reached for 19% of Nb_2O_5. Surface niobia species on alumina exhibit peculiar and specific properties [11,12]. However, the potentialities of a metal like platinum supported on this type of support were not yet well characterized in the literature. The influence of the preparation method on the structure of metallic particles, the degree of SMSI and catalytic properties of Pt/Nb_2O_5 and $Pt/Nb_2O_5/Al_2O_3$ were investigated. These systems were characterized by temperature-programmed reduction (TPR), hydrogen and carbon monoxide chemisorption and UV-Vis spectroscopy. The catalytic activity and selectivity were evaluated by *n*-heptane dehydrogenation.

2. Experimental

2.1. Catalyst preparation

Pt/Nb_2O_5 catalysts were prepared by ion-exchange (Pt/Nb_2O_5-IE) or incipient wetness techniques (Pt/Nb_2O_5-IW). The platinum loading was 1% (w/w) in both catalysts.

Niobia support (BET area=65 m^2/g) was obtained by calcination of niobic acid (CBMM – HY 340) at 773 K for 2 h.

The ion exchange was performed using a solution of $Pt(NH_3)_4Cl_2$ (Aldrich) and NH_4OH (1 N) with pH 10. The support was added to the solution and stirred for 4 h. Then, the suspension was filtered and washed with deionized water. The samples were dried at 393 K, and calcined in air at 573 or 773 K for 2 h.

Pt/Nb_2O_5-IW was prepared by the conventional incipient wetness method, 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.

Nb_2O_5/Al_2O_3 supports were prepared by impregnation over alumina powder (Harshaw, BET area: 200 m^2/g) with an oxalic acid solution of niobium oxalate (pH=0.5), dried at 393 K for 16 h and calcined at 823 K for 16 h. The niobia loading were 0%, 1%, 5%, 10% and 20% (w/w). Platinum (1% w/w) was added by incipient wetness with an aqueous solution of H_2PtCl_6 (Reagen), followed by drying at 393 K for 16 h and calcination in air at 803 K. These catalysts are codified as 1P*x*NA, where *x* represents the loading of niobia (w/w).

2.2. TPR

The TPR apparatus and methodology were described elsewhere [13]. The precursors were dehydrated at 393 K under flowing Ar before the reduction. A mixture of 1.5% hydrogen in argon flows at 30 ml/min through the sample, raising the temperature at a heating rate of 10 K/min up to 773 K.

2.3. Diffuse reflectance UV-Vis spectroscopy

The samples were analyzed 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 of the support, the reflectance r (λ) was rated to the reflectance of the support and the results were calculated as function of Shultz Kubelka–Munk equation.

2.4. Chemisorption measurements

Carbon monoxide and hydrogen uptakes were obtained using an automatic adsorption system (ASAP 2900, Micromeritcs). After reduction at 573 or 773 K under H_2 flow, the samples were evacuated at 10^{-6} Torr for 30 min at the reduction temperature and cooled to room temperature. Irreversible H_2 uptakes were obtained from the total and reversible adsorption isotherms.

Infrared spectra of adsorbed CO_2 were taken at 50 Torr and room temperature using a Perkin–Elmer model 2000 FTIR in a resolution of 2 cm^{-1}. Samples for infrared spectroscopy were in the form of self-supporting disks and weighed around 25 mg. The Nb_2O_5/Al_2O_3 catalysts were heated at 473 K under vacuum at least 10^{-5} bar. The CO_2 uptake was calculated and normalized related to alumina after integration of the peaks. These results allowed the determination of the surface coverage of the niobium oxide overlayer since CO_2 titrates the basic surface hydroxyls [14].

Infrared spectra of adsorbed pyridine (Perkin–Elmer model 2000 FTIR in a resolution of 2 cm^{-1}) were taken after chemisorption of pyridine at 423 K on the catalysts pretreated at 703 K under vacuum (10^{-5} bar). The samples were in the form of self-supporting disks and weighed around 25 mg.

2.5. Catalytic activity

The dehydrogenation of *n*-heptane was carried out in an atmospheric glass microreactor. The sample was dried at 393 K for 30 min under flowing N_2, followed by reduction in a H_2 flow at 773 K for 30 min. The reaction mixture was obtained flowing H_2 through 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 by using a gas chromatograph equipped with a flame ionization detector and a 50 m KCl–Al_2O_3 capillary column. After 4 h in time on stream, the mixture flow was changed and the selectivity was compared at the same range of conversion (10–15%).

3. Results and discussion

Fig. 1 shows the surface coverage of niobia overlayer as function of the niobia loading, measured by infrared of chemisorbed CO_2. The fraction coverage reached a saturation point around 10% of niobia loading, and remained constant with increasing niobia contents. These results are similar to the obtained by Jehng and Wachs [11] although the coverage was not complete here.

The TPR profiles of the catalysts are displayed on Fig. 2. Pt/Nb_2O_5-IE catalyst calcined at 773 K, exhibits a maximum peak at 383 K, which is related to the reduction of platinum oxide and a broad shoulder around 473 K. The H_2 uptake observed around 650 K is attributed to the reduction of Nb_2O_5 [8]. The Pt/Nb_2O_5-IW profile is very similar unless an additional reduction peak at room temperature

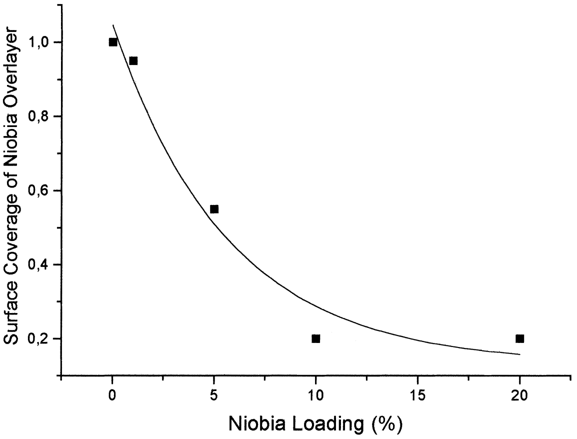

Fig. 1. Surface coverage of niobia overlayer.

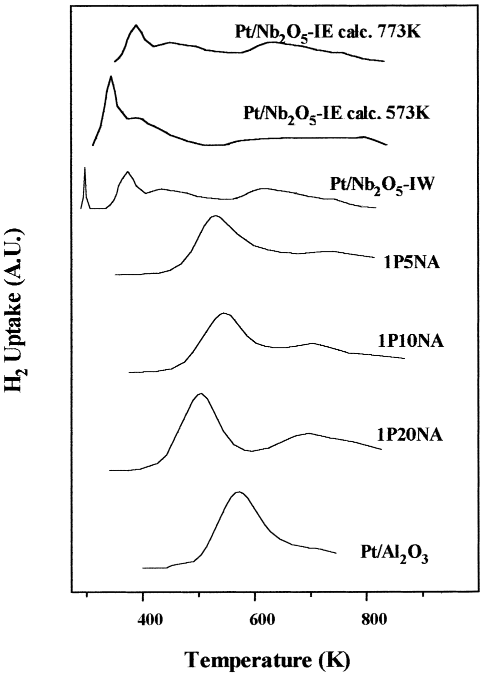

Fig. 2. Temperature programmed reduction profiles of platinum catalysts.

ascribed to PtO_2 bulk. The Pt/Nb_2O_5-IE catalyst presents a higher H_2 uptake after calcination at 573 K than after 773 K, due to the reduction of the platinum precursor (peak at 360 K), which indicates that at 773 K, partial reduction of platinum occurs during the calcination step, probably due to the formation of NH_3 during the decomposition of the platinum salt ($(NH_3)_4PtCl_2$). The TPR profiles of $Pt/Nb_2O_5/Al_2O_3$ samples are very similar. All samples displayed a peak around 560 K, which is related to the formation of an oxychloroplatinum surface complex, already observed on Pt/Al_2O_3 catalysts, prepared by incipient wetness with a H_2PtCl_6 solution [15]. The samples with higher niobia loading exhibit a small peak shift of the maximum to lower temperatures, which can be explained by a lower amount of chlorine retained on the support, since an increasing amount of niobia covers the alumina surface. It also displays the reduction of Nb_2O_5 at high temperatures.

Fig. 3 presents the UV-Vis DRS spectra of different catalysts. The Pt/Nb_2O_5-IW and Pt/Nb_2O_5-IE calcined at 773 K exhibit a band at 410 nm, which can be ascribed to the presence of platinum oxide (α-PtO_2). All the Nb_2O_5/Al_2O_3 supported catalysts present a band in the metal-ligand charge transfer range, varying from 320 to 360 nm, depending on the niobia content. This band is very similar to the observed in the Pt/Al_2O_3 catalysts, which can be attributed to the formation of PtO_xCl_y surface complex, confirming the TPR results. The intensity of the CT band decreases for higher niobia loading and vanishes on the Pt/Nb_2O_5 catalysts. These results can be explained based on the specific capacity of alumina to retain chlorine ions [15]. In fact, both chloride precursors did not allow stable formation of PtO_xCl_y species on Pt/Nb_2O_5 catalysts.

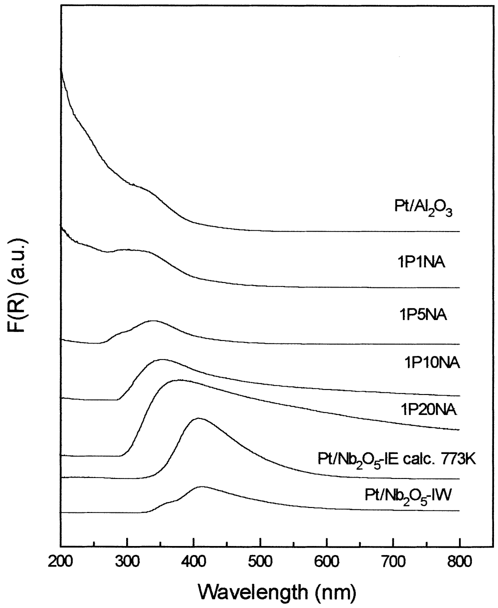

Fig. 3. DRS-UV-Vis spectra of calcined platinum catalysts.

The chemisorption results are shown in Table 1. After reduction at 573 K, the Pt/Nb_2O_5 catalysts present low H/Pt and CO/Pt values. These results are very similar for the samples prepared by incipient wetness and by ion exchange, calcined at 773 K. This is not surprising, since at 573 K the SMSI may be already occurring. Besides, DRS data indicate the platinum precursors present a small amount of chlorine attached to the metal on niobia, resulting in low dispersed platinum particles [15]. After reduction at 773 K,

Table 1
H_2 and CO chemisorption on Pt catalysts

Catalyst	Reduction at 573 K				Reduction at 773 K			
	H_2 uptake (μmol/g cat)	H/Pt	CO uptake (μmol/g cat)	CO/Pt	H_2 uptake (μmol/g cat)	H/Pt	CO uptake (μmol/g cat)	CO/Pt
Pt/Nb_2O_5-IW	7.0	0.27	15.6	0.30	1.3	0.051	3.0	0.06
Pt/Nb_2O_5-IE (calc. 773K)	3.2	0.12	6.2	0.12	—	—	0.49	0.007
Pt/Al_2O_3	25.4	0.993	41.8	0.815	23.0	0.896	36.2	0.707
1P1NA	18.2	0.712	28.7	0.559	16.0	0.623	25.9	0.506
1P5NA	18.7	0.730	36.8	0.717	12.8	0.50	28.6	0.558
1P10NA	16.2	0.634	33.3	0.649	3.6	0.139	21.7	0.424
1P20NA	5.4	0.209	11.3	0.220	0.3	0.012	6.0	0.118

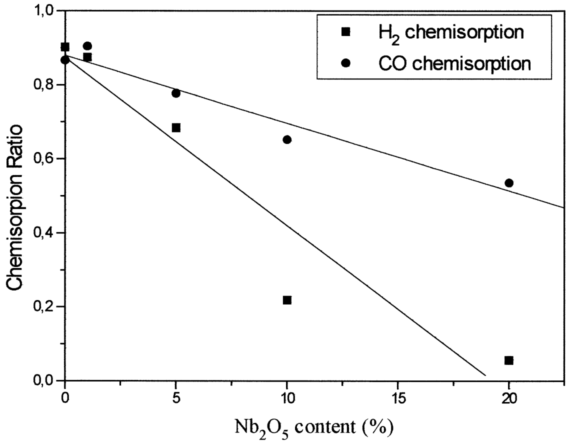

Fig. 4. Ratio between gas chemisorption uptake after reduction at 773 K and after reduction at 573 K in function of Nb_2O_5 content.

the amount of hydrogen and carbon monoxide chemisorption decreases strongly, which is attributed to the SMSI effect promoted by the niobia reduction, as also observed in the TPR profiles. On the other hand, the samples supported on Nb_2O_5/Al_2O_3 after reduction at 573 K present higher chemisorption values of H/Pt and CO/Pt than the Pt/Nb_2O_5 catalyst. This can be explained observing the DRS and TPR results: after calcination, since the main surface precursor on those samples is PtO_xCl_y which promotes high dispersions on the Pt/Al_2O_3 catalysts. After reduction at 773 K, the adsorption capacity on platinum decreases and this is more pronounced with increasing niobia contents. Fig. 4 exhibits the ratio of adsorbed gas after reduction at 773 and 573 K with the niobia loading. It shows that the SMSI is more influenced by the hydrogen chemisorption than the CO chemisorption, although both gases are influenced by the support reduction, which is explained by a higher hydrogen ensemble demand for adsorption than the required by carbon monoxide.

The conversion of *n*-heptane results are presented in Fig. 5. The Pt/Nb_2O_5 samples show a low initial activity that deactivates quite fast. The Nb_2O_5/Al_2O_3 supported catalysts present higher initial activities and are more stable than the Nb_2O_5 supported catalysts. Furthermore, the samples with higher niobia loading showed a high selectivity towards olefins. As compared to $Pt–Sn/Al_2O_3$ catalysts [9] $Pt/Nb_2O_5/Al_2O_3$ catalysts presented a higher olefin to aromatics ratio. The low initial conversion is attributed to the lower dispersion of platinum and the partial coverage by reduced NbO_x species.

However, the higher stability observed in the $Pt/Nb_2O_5/Al_2O_3$ catalysts compared to the Pt/Nb_2O_5 needs a better explanation model. The deactivation by coke in the hydrocarbon conversion is described by two main mechanism: the poliene and the C1 routes [16]. The former route favors the olefins coupling

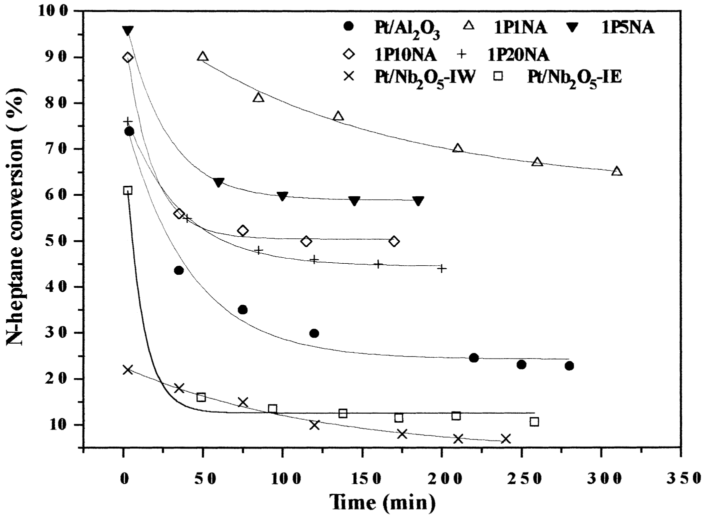

Fig. 5. Conversion of *n*-heptane at 773 K.

Table 2
Selectivity for *n*-heptane conversion at 773 K on platinum catalysts (P=1 atm; H_2/C_7H_{16}=16)

Catalyst	Hydrog. [a]	Hydrocrack. [b]	C_7 olef [c]	Tol. [d]	Isom. [e]	R [f]
Pt/Nb_2O_5-IW	7	—	65	5	23	13
Pt/Nb_2O_5-IE (calc. 773 K)	17	3	68	3	9	22.7
Pt/Al_2O_3	32	13	17	32	6	0.5
1P1NA	18	15	48	12	7	4
1P5NA	14	15	48	12	11	4
1P10NA	4	1	82	6	7	13.7
1P20NA	3	2	78	8	9	9.8
1Pt1SnA [g]	2	2	63	18	15	3.5

[a] Selectivity to hydrogenolysis products.
[b] Selectivity to hydrocracking products.
[c] Selectivity to C_7 olefins.
[d] Selectivity to toluene.
[e] Selectivity to heptane isomers.
[f] Ratio between the selectivity to olefins and the selectivity to toluene.
[g] Ref. [9]

promoted by acidic sites, while the C1 mechanism the carbon deposition on metallic sites from light molecules, as methane. The low selectivity towards hydrogenolysis products (Table 2) indicates that the C1 route is less probable on niobia based catalysts. This induces that the deactivation process is related to the acidity of the support.

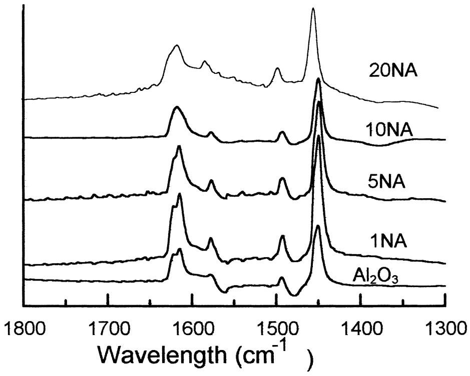

Fig. 6. Infrared spectra of pyridine adsorbed on Nb_2O_5/Al_2O_3 catalysts.

Fig. 6 presents the infrared spectra of adsorbed pyridine on the several catalysts, while Table 3 lists the distribution of Lewis and Brönsted acid sites, calculated by the integration of the bands at 1453 cm^{-1} (Lewis sites) and at 1493 cm^{-1} (Lewis and Brönsted sites). The amount of Lewis acid sites is maximum for the catalysts containing 1% niobia, and decreases for higher niobia loadings. The ratio between Lewis acid sites and the total acid sites decreases with the niobia loading, indicating the formation of Brönsted acid sites. These results are in agreement with the work of Jehng and Wachs [11], who have shown that the Brönsted acidity of Nb_2O_5/Al_2O_3 samples increases with the niobia loading. This is attributed to the tetrahedral or octahedral niobia units containing Nb=O bands [17] dispersed on alumina surface. On the other side, the niobia calcined at 773 K displays few and weak acidic sites [9]. Davis et al. [18] presented a model which indicates that the

Table 3
Lewis acid sites (LAS) and Brönsted acid sites (BAS) determined by pyridine adsorption

	Al_2O_3	1NA	5NA	10NA	20NA
LAS [a]	0.255	0.348	0.308	0.211	0.214
LAS/(LAS+BAS) [b]	12.48	11.4	10.064	8.39	7.01

[a] Obtained by integration of the peak at 1453 cm^{-1}/mg of catalyst.
[b] Ratio of integrated peaks at 1453 cm^{-1} (LAS) and at 1493 cm^{-1} (LAS+BAS).

Brönsted acidic sites are very important to 'drain-off' the coke precursors produced on metallic sites cleaning up the surface. The Pt/Nb_2O_5 catalysts show high selectivity towards olefins, as presented in Table 2. The hydrogenolysis selectivity decreases, since the SMSI effect causes dilution of metallic particles. Besides, the lower acidity of this support promotes lower amounts of hydrocracking, isomerization and aromatization products. However, the higher olefin density localized on metal sites, as observed by TPO of deactivated catalysts [19] is responsible for a faster deactivation.

The $Pt/Nb_2O_5/Al_2O_3$ catalysts present two different possibilities:

1. At low niobia contents (1–5%), hydrocracking occurs on Lewis acidic sites decreasing the selectivity towards olefins. Furthermore, hydrogenolysis occurs on larger ensembles of platinum;
2. At high niobia loading (10–20%), the SMSI intensity is higher and the diluted metallic ensembles allow to minimize the hydrogenolysis reactions. In addition, the Lewis acidity decreases [11] preventing hydrocracking, while the Brönsted sites attract coke precursors to the support and therefore free metallic sites for the dehydrogenation, thus resulting more stable catalysts.

4. Conclusions

The Nb_2O_5 and Nb_2O_5/Al_2O_3 supported Pt catalysts investigation in this work allows us to conclude that different precursors are formed depending of the support. The $Pt/Nb_2O_5/Al_2O_3$ catalysts present PtO_xCl_y surface complexes, leading to small metallic particle sizes, while the Pt/Nb_2O_5 catalysts favors the formation of large particles sizes, the last one prepared by incipient wetness and ion exchange.

The niobia containing catalysts are very selective to the formation of olefins in the *n*-heptane conversion, which could be explained by the dilution of platinum atoms by reduced niobia species after reduction at 773 K. The $Pt/Nb_2O_5/Al_2O_3$ catalysts present very high stability compared to the Pt/Al_2O_3 and Pt/Nb_2O_5 catalysts, which is consistent with the formation of Brönsted sites on Nb_2O_5/Al_2O_3 systems.

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