ON THE PREPARATION OF Ni–La SUPPORTED ON SILICA BY SOL-GEL PROCESS VIA PROPIONATES

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Abstract

Ni–La/SiO_2 catalysts were prepared by using a new metal organic precursor $M(OC_3H_7)n$, dissolved in organic solvent, hydrolysed and finally condensed to form inorganic polymers containing M–O–M or M–(μOH)–M linkages. An optimal distribution of both the active phase 'Ni' and the promoter 'La_2O_3' was ensured by addition of their corresponding salts, previously dissolved in propionic acid, to a silica solution prior to gelation. After drying under vacuum the precursor was submitted to thermal treatment in air at 600°C with a heating rate of 1°C min^{-1}.

The precursors and the corresponding catalysts were characterised by various techniques (TG-DTA, XRD, FTIR, TEM, BET and porosimetry) and tested for methane dry reforming.

Keywords: Ni–La–Si–O system, methane dry reforming, sol-gel preparation

Introduction

Catalysts composed by metal oxides supported on inorganic materials, can be prepared by the impregnation with aqueous or organic solvents, or chemical vapour deposition (CVD), whereas those composed by bulk mixed oxide systems can be obtained following several different procedures. Among the oxides, Al_2O_3 and SiO_2 are widely used as support in heterogeneous catalysis [1]; for example supported metallic oxides show high activity and selectivity after H_2 reduction. The intrinsic catalytic activity is often related to the active species dispersion on the support [2]. Moreover, the structure or phase composition of silica or alumina supported nickel catalysts are well known, and metallic nickel particles have been proposed as the active phase for methane dry reforming [2–4].

Dealing with supported metal catalysts, it is generally believed that chemical properties as redox potential and acid-base behaviour of the support are directly responsible for the catalytic action and that these properties are enhanced or modified by the preparation method.

In this work we report a novel sol-gel route [5] that has been developed to prepare a three-component catalyst consisting of supported Ni on silica and promoted

with lanthanum, where the intermediate metal oxides are homogeneously distributed in the silica matrix. The reported procedure results from several attempts carried out under different experimental conditions, using as starting materials: $Si(OMe)_4$, $Si(OEt)_4$, La_2O_3 and $Ni(OH)_2–NiCO_3$.

The effect of the preparation method on the redox properties of the Ni, as such or promoted with La_2O_3 and the catalytic tests with methane dry reforming were performed by varying the Ni/La ratio.

Experimental

Sol-gel preparation

The catalyst was prepared (Fig. 1) by dissolving separately at 85°C, Ni carbonate basic hydrate (purum Fluka), basic lanthanum oxide La_2O_3 (purum Fluka) and $Si(OCH_3)_4$ (Aldrich 99%) or $Si(OC_2H_5)_4$ (Aldrich 99%) under constant stirring in liquid propionic acid (Aldrich 99%). The dissolution of the Ni and La compounds is very slow, after some hours the solutions become transparent. Particularly for the lanthanum solution it was necessary to use a starting material of high purity in order to increase the dissolution rate of the lanthanum oxide which took place after a long period under acidic conditions. The above solutions were then mixed and hydrolysed with a few drops of distilled water and evaporated at 50°C under vacuum (10^{-2} atm); the obtained gel (a polymer composed of M–O–M or M–(μOH)–M bonds) was frozen with liquid nitrogen, thus powdering the gel (Ni, La and Si-propionate precursor) into solid state.
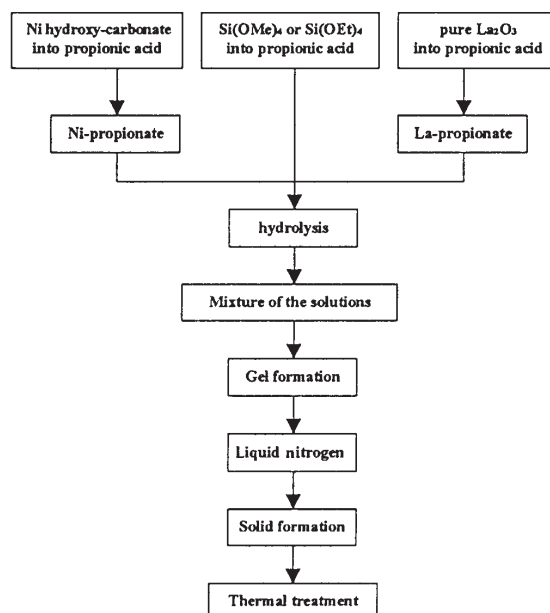

Fig. 1 Summarised Ni–La/SiO_2 catalyst preparation by sol-gel method

Similarly, Ni propionate precursor (NiPP) and La propionate precursor LaPP are obtained with the sol-gel procedure.

Impregnated catalyst preparation

Catalysts were prepared by consecutive incipient wetness-calcination procedure which allows to obtain high metal accessibility even at lower loads on silica with high surface area. The preparation was carried out by using SiO_2 (Merck, 70–230 mesh) and solutions of $Ni(NO_3)_2 \cdot 6H_2O$ (purum Fluka) and $La(NO_3)_3 \cdot 6H_2O$ (puriss Fluka) which correspond to the percentages of Ni and La desired. The solution containing the desired salts was brought into contact with wet silica, under vacuum by using a Rotavapor, at 333 K. The first step of the impregnation consists in wetting the silica with distilled water then the solution containing Ni or La salts is added dropwise while rotating the flask containing the silica in order to have a homogeneous and superficial deposition of the promoter.

After cooling, the catalyst was brought to atmospheric pressure, it was dried at 333 K under argon, and then heated at 433 K for 6 h. In the case of Ni–La–Si catalyst, the Ni–SiO_2 catalyst was impregnated with a lanthanum salt in the same way, before calcination under air at 823 K for 6 h.

Characterisation

The evolution of the decomposition of the precursors was studied under air using a Seiko Instruments Thermogravimetric Analyser (TG-DTA-DTG). The samples, weighing approximately 20 mg, were placed in quartz crucible and heated up to 600°C (1–5°C min^{-1}). The gas feed was 6 l h^{-1}.

Porosimetry and B.E.T. surface measurement were performed on a Quantasorb (Quantachrome Co) instrument.

XRD spectra were obtained by a Philips PW 1050 using the CuK_α radiation.

TEM investigations analyses were performed with a Philips CM 30 microscope.

FT-IR measurement were performed using a Perkin Elmer Mod. 1760 (KBr pellets).

Catalytic apparatus

A quartz tube microreactor (10 mm in diameter, 400 mm overall length) system was used to study the activity and selectivity of the supported catalysts [6]. The catalyst (200–500 mg) were placed in the central zone of the reactor between two layers of carborundum. The catalytic activity of both unreduced and reduced catalysts was determined by monitoring the effluent concentration of reagents and products using a GC (Dani 3800) equipped with a Thermal Conductivity Detector and a column packed with Carbosieve S II. CO_2, CH_4 and CO_2+CH_4 pulses (1 ml; 85% reactants and 15% of N_2 used as an internal reference) were injected at controlled rate in a He carrier stream. Samples (1 ml each) of the effluent gases were collected every 6 s with a heated Valco 16 multiport valve. Measurements of the amount of deposited coke

were made by extensive hydrogenation and measuring the total methane production after each experiment.

Results and discussion

Thermal activation of the precursor

The behaviour of the Ni–La/SiO$_2$ propionate precursor during thermal activation and consequently the phase composition of the final catalyst, can be better understood if the decomposition patterns of the simple nickel and lanthanum propionate are taken into account.

Ni propionate precursor (NiPP)

The decomposition of Ni propionate under air (Fig. 2a) shows two endothermic peaks between ambient temperature and 110°C. The first one is attributed to a mass loss of ca 19.3% (H$_2$O) while the second peak (27.4% mass loss) indicates a transformation of C$_3$H$_7$O groups into C$_2$H$_5$O ones as evidenced by mass spectra analyses. The two peaks are followed by an exothermic peak at 311°C which can be attributed to the decomposition of propionate groups and crystallisation of NiO. The heat produced during this exothermic phenomenon corresponds to ca –3.98 kJ g^{-1}. The total mass loss of the decomposition of NiPP was estimated to be 83.3%.
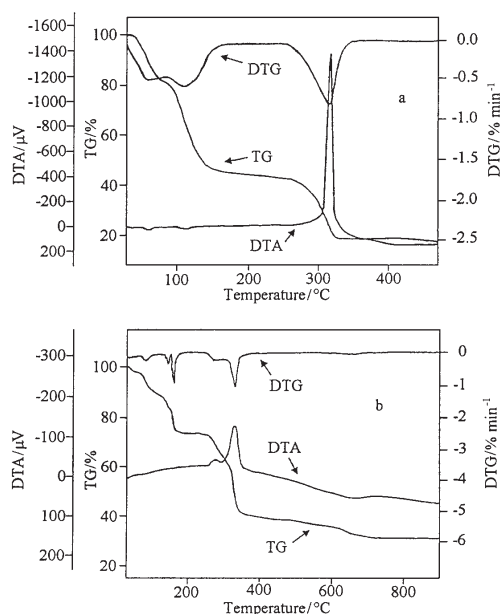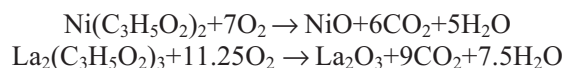

Fig. 2 Decomposition under air of the sol-gel precursor a – NiPP, b – LaPP

La propionate precursor (LaPP)

Under air the decomposition of LaPP (Fig. 2b) shows an endothermic peak accompanied by a mass loss of 10.1% (H_2O), followed by a second mass loss of about 15.7% related to the loss of free propionic acid. A sharp exothermic peak at 326°C (mass loss of 34.7%) is due to the simultaneous decomposition of propionate groups and crystallisation of lanthanum oxide. This peak is preceded by a small exothermic peak at ca 235°C which is due to the formation of CH_3CH_2O or $CH_3CH_2CO_2$ radicals [7]. The precursor heat decomposition at 326°C was estimated to be -10 kJ g^{-1}. The total mass loss during the LaPP decomposition was found to be 67.8%.

The overall decomposition process of the NiPP and LaPP can be exemplified by the following equations:

$$Ni(C_3H_5O_2)_2 + 7O_2 \rightarrow NiO + 6CO_2 + 5H_2O$$
$$La_2(C_3H_5O_2)_3 + 11.25O_2 \rightarrow La_2O_3 + 9CO_2 + 7.5H_2O$$

In air the percentage of mass loss during the decomposition of NiPP (between 110 and 425°C) and LaPP precursors (between 180 and 600°C) are 64% (63.5% theoretical) and 34.7% (34.4% theoretical) respectively in agreement with the cited equations.

Ni–La/SiO$_2$-propionate precursor (NiLaSiPP)

The Ni–La/SiO$_2$-propionate precursor was then treated under air from 25 to 600°C. Due to this activation, only traces of Ni oxide phase were observed on the SiO$_2$. The Ni–La/SiO$_2$ activation step is more important as it determines directly the catalytic performance of the catalyst.

The TG-DTA analyses (Fig. 3b) show that in presence of air and after ethoxy groups removal, the decomposition of NiLaSiPP leads to two phenomena which can take place simultaneously: propionate groups oxidation and Ni(II) oxide crystallisation on amorphous silica.

In order to elucidate all the different thermal effects and at the same time avoiding excessive heat-flow or the ignition of explosive reactions occurring at 200–350°C, the heating rate was reduced to 1°C min^{-1}.

The main endothermic peak characterised by an abrupt mass loss of ca 90% occurred below 100°C. This is then followed by a slight mass loss (ca 0.7%) accompanied by an exothermic peak at ca 310°C associated to the residual propionate group in crystalline phase at high temperatures. Molecular mass of these organic compounds were evaluated by mass spectroscopy in the range of 45 to 74 ((CH_3CH_2O), and traces of ($CH_3CH_2CO_2$) and ($CH_3CH_2CO_2H$)). This exothermic peak corresponds also to the formation of nickel oxide since the temperature at which this phenomenon occurs is the same obtained for nickel propionate precursor (NiPP) (Fig. 2a). No other exothermic peak characteristic of lanthanum oxide crystallisation was detected, probably due to the lower lanthanum oxide content (0.8 to 2% mass). Comparing Ni–La/SiO$_2$-propionate precursor (NiLaSiPP) (Fig. 3b) with Ni/SiO$_2$-propionate precursor (NiSiPP) (Fig. 3a) similar decomposition were obtained.
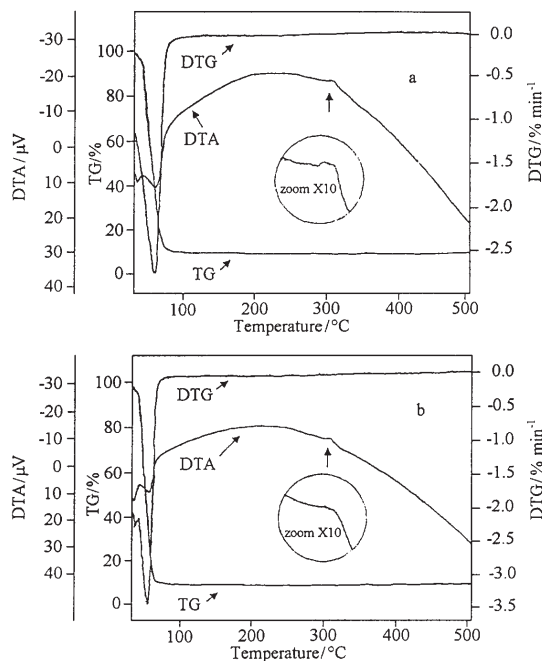
Fig. 3 Decomposition under air of the sol-gel precursor a – NiSiPP, b – NiLaSiPP

The thermogravimetric analyses performed under air (Fig. 3a), indicate that the initial mass loss (ca 6.5%) is followed by an abrupt increase of mass loss (ca 83.5%). Similar to (NiPP) (Fig. 2a), a mass loss of ca 0.7% was detected at ca 308°C and it is due to the oxidation of the organic groups (propionate ligands). The total mass loss for (NiSiPP) and (NiLaSiPP) during the decomposition of the sol-gel precursor can be estimated to be 88.2 and 91.7% respectively.

Comparing the IR spectra of NiPP and LaPP with those of NiLaSiPP (Fig. 4a,b,c), it can be seen that the spectra of NiPP (Fig. 4a) is quite similar to that of LaPP (Fig. 4b); but differs from NiLaSiPP (Fig. 4c) spectrum. This difference is due to the low number of propionate groups corresponding to lanthanum and nickel content in the catalyst. The observed peak at 1100 cm^{-1} and the shoulder at 1200 cm^{-1} of amorphous silica partly mask the small peaks characteristic of the propionate groups.

The overall decomposition process of the Ni–La/SiO$_2$-propionate precursor (NiLaSiPP) can thus be exemplified by the following equation:

$$Ni(C_3H_5O_2)_2La_2(C_3H_5O_2)_3/Si(OC_2H_5)_4 + 30.25O_2 \rightarrow$$
$$NiO-La_2O_3/SiO_2 + 23CO_2 + 22.5H_2O$$
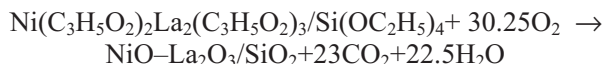
In Table 1, it is reported the surface specific area of all the samples prepared by sol-gel (sg) or by impregnation (imp) techniques. It can be noticed that the (sg) catalysts BET surface area is higher than that of the corresponding (imp) catalysts (Table 1), thus the distribution of Ni metallic atoms on the exposed surface is definitely
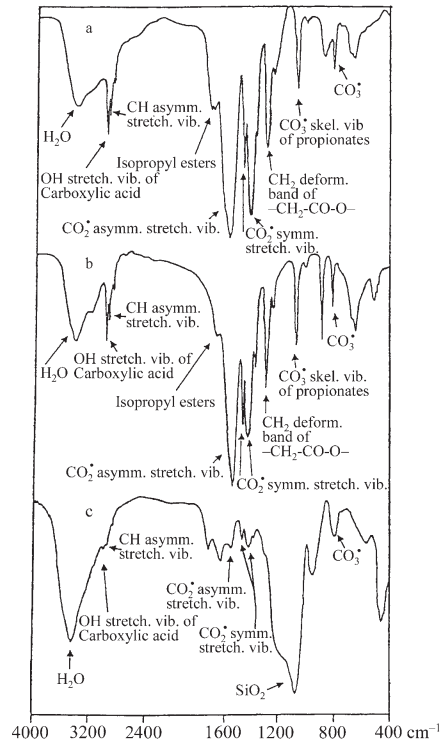
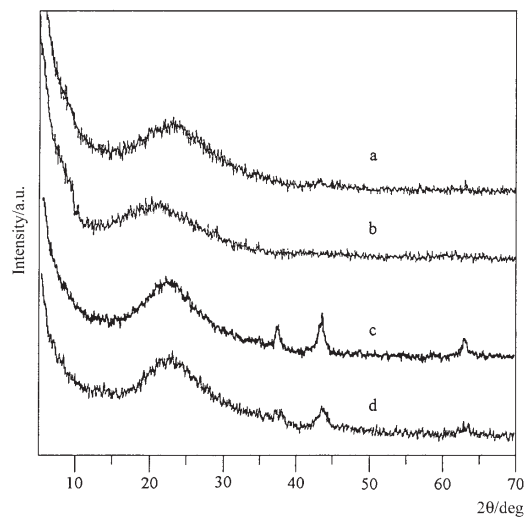**Fig. 4** FTIR spectra of the sol-gel precursor a – NiPP, b – LaPP, c – NiLaSiPP

Fig. 5 XRD spectra of catalysts a – (sg) 4%Ni/SiO$_2$, b – (sg) 4%Ni–2%La/SiO$_2$, c – (imp) 5%Ni/SiO$_2$, d – (imp) 3.5%Ni–2.5%La/SiO$_2$

higher with respect to the impregnated catalyst. NiO peaks were not detected by XRD analyses (Fig. 5) after calcination of (sg) catalysts at 873 K for 2 h.

Table 1 Comparison of phase composition and specific surface area of prepared catalysts

Catalyst obtained by	Ni/La experimental[*]/mass%	$S_{BET}/m^2\ g^{-1}$
Sol-gel technique (sg)		
SiO_2	–	797
4%Ni/SiO_2	3.43Ni/0	775
4%Ni–0.85%La/SiO_2	2.96Ni/0.89La	709
4%Ni–1.3%La/SiO_2	3.16Ni/1.11La	666
4%Ni–2.0%La/SiO_2	3.01Ni/1.93La	657
Wet impregnation (imp)		
SiO_2[**]	–	430
5%Ni/SiO_2	4.71/0	285
3.5%Ni–2.5%La/SiO_2	3.20/2.35	320
5%Ni–1%La/SiO_2	4.31/0.88	302
5%Ni–1.5%La/SiO_2	4.43/1.61	252
5%Ni–3.5%La/SiO_2	4.65/3.22	228

[*]Measured by atomic absorption
[**]Merck 7754, high purity 70–230 mesh, 60 Ĺ, 63–200 μ

The catalysts activated under air show an infrared absorption band at 975 cm^{-1}. This band can be assigned to Si–O vibrations of the Ni–O–Si group, since absorption bands characteristic of the metal–O–Si groups appear in the 900–1100 cm^{-1} region, e.g. 1050 cm^{-1} for Al [8] 1018 cm^{-1} for Zr and 920 cm^{-1} for Ti [9]. The relative intensity of the band at 975 cm^{-1} increased with the nickel concentration in the catalyst. These results seem to indicate that nickel atoms dispersed on the silica form chemical bonds with oxygen atoms in the support. This implies that after the (sg) catalyst reduction under hydrogen only some of nickel was reduced while the rest remained bonded to oxygen atoms in the carrier forming Ni–O–Si bonds.

On the contrary, the XRD of the (imp) catalysts have shown that the detection of nickel is still possible down to ca 2.3%. It should also be noticed that if the impregnation is made according to the traditional mode, incipient wetness on dry silica, the detection limit of nickel XRD is ca 7%. Figure 5 reports the XRD spectra of 5% Ni/SiO_2 and 3.5% Ni-2.5% La/SiO_2 (imp) catalyst.

Following these observations and IR data obtained after catalysts reduction (not reported) it is reasonable to think that in the case of (sg) catalysts only a small part of nickel is present on the surface suggesting that the sol-gel technique yields uniform distribution of Ni inside the SiO_2 matrix.

Adsorption of small amounts of H$_2$ (μmol g^{-1}) on the (sg) catalysts was observed after reduction with hydrogen at 873 K, regardless of the higher distribution and smaller particle size (5–8 nm determined by TEM analyses) of metallic nickel. On the

Table 2 CO_2 plus CH_4 pulse with sol-gel (sg) and impregnated (imp) reduced catalysts

Catalyst	CH_4 conv./	CO_2 conv./	C balance/	CO yield/	TOF_{CO}/ s^{-1}	Ni metallic surface[*]/ $m^2 g^{-1}$	Percentage of deactivation[**]/% h^{-1}
		%					
(sg)4%Ni/SiO$_2$	21.0	29.9	0.1	25.5	1.37	0.69	1.0
(imp)5%Ni/SiO$_2$	83.9	21.5	7.5	49.6	0.96	1.91	1.1
(sg)4%Ni-2%La/SiO$_2$	90.0	75.1	−6.0	88.3	14.31	0.23	3.3
(imp)5%Ni-3.5%La/SiO$_2$	88.7	59.5	−2.9	76.1	5.02	0.58	9.0

T=600°C, (CO_2+CH_4) pulse=1 ml (85% reactants and 15% N_2)
[*]Determined according to the literature procedure [12]
[**]Measured in continuous mode using the same operating conditions (T, contact time τ and reagents concentrations) as in pulse mode

contrary in the case of (imp) catalysts, where metallic Ni (27–32 nm) is almost entirely attached on the support surface, the amounts of H_2 adsorbed was found to be higher than that of the corresponding (sg) catalysts. H_2 µmol g^{-1} adsorbed on the (sg)/ (H_2 µmol g^{-1}) adsorbed on the (imp) catalysts ratio is ca 0.6 in agreement with findings reported in the literature for Ni–Al_2O_3 prepared by sol gel technique [10].

The pore volumes and the mean pore radius of the impregnated and sol-gel catalysts were 0.4, 1.4 cm^3 g^{-1} and 38, 25 Ĺ respectively.

Catalytic results

The catalytic activity data measured at 600°C for 4% Ni/SiO_2, 4% Ni–2% La/SiO_2 sol-gel (sg) and the corresponding impregnated systems (imp) are reported for comparison in Table 2.

With respect to the (imp) systems, (sg) catalysts gave different results in terms of CO_2 conversion and CO yield especially in presence of lanthanum oxide. These differences are probably due to both the moderate basicity of La_2O_3, that favours CO_2 adsorption, and to the interfacial effects [12] between metallic nickel and lanthanum oxide (homogeneously mixed owing to the preparation method) on the support surface.

When the activity is expressed in terms of TOF (turn over frequency s^{-1}) better performances are obtained with (sg) catalysts (Table 2).

The catalytic performance of (sg) systems can also be explained in terms of CO_2 reactivity and of very low coking during the CH_4–CO_2 reaction together with a stable activity and very low sintering of Ni. In fact, it was experimentally observed that the deactivation process and the life time of the (sg) and (imp) catalysts are different. Catalysts comparison show that the percentage of deactivation *vs.* time is sensibly higher with (imp) catalyst especially in the case of La-doped catalysts (Table 2). After only 8 h on stream using (imp) catalysts carbon deposition leads to reactor blocking (high drop pressure) while for sol-gel catalysts this does not occur.

Finally, the recovery of deactivated catalysts (imp) and (sg) tested under the same reaction conditions, in presence of air, leads to the elimination of carbon by a combustion reaction (either deposited carbon or carbon whiskers), while regeneration under reducing atmosphere (H_2) was possible with (sg) catalysts.

These high performance for CO_2 reforming of methane on (sg) catalyst must, therefore, be due to both the fine and uniform metallic Ni particles and to La_2O_3 promoter distributions throughout silica matrix. The uniform distribution of La_2O_3 is ensured by the sol-gel preparation. In addition the catalysts promotion with La_2O_3 tends to reduce coking with respect to reforming and this is more pronounced in the case of (sg) promoted catalysts.

Conclusions

We have synthesised a Ni–La–Si precursor developing a new sol-gel methodology via propionates, which allows to obtain three components nickel-lanthanum-doped silica catalyst.

A peculiarity of this preparation procedure is the possibility to obtain a relevant and homogeneous distribution of the Ni and La_2O_3 promoter. The distribution improves the lanthanum-nickel interaction which probably leads to the creation of a new type of synergetic sites at the $Ni–La_2O_3$ interfacial area giving a better activity.

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