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Abstract: Three activated carbons (ACs) having apparent surface areas higher than 2500 m²/g were doped with nitrogen by treatment with urea at 623K under air flow. Nitrogen contents as high as 15.1 wt.% were obtained, but resulting in decreased surface areas and pore volumes. Hydrogen storage capacities of ACs before and after nitrogen doping were measured at 77K and up to 8MPa. After doping, the hydrogen uptake was lower due to the corresponding decrease of surface area. Statistical, ANOVA, analysis of the relevancy of surface area and nitrogen content on hydrogen storage at 77 K was carried out, taking into account our data and those data available in the open literature. We concluded that surface area controls hydrogen adsorption and nitrogen content is not a relevant parameter.

Hydrogen uptake of high surface area-activated carbons doped with nitrogen

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Abstract

Three activated carbons (ACs) having apparent surface areas higher than 2500 m²/g were doped with nitrogen by treatment with urea at 623K under air flow. Nitrogen contents as high as 15.1 wt.% were obtained, but resulting in decreased surface areas and pore volumes. Hydrogen storage capacities of ACs before and after nitrogen doping were measured at 77K and up to 8MPa. After doping, the hydrogen uptake was lower due to the corresponding decrease of surface area. Statistical, ANOVA, analysis of the relevancy of surface area and nitrogen content on hydrogen storage at 77 K was carried out, taking into account our data and those data available in the open literature. We concluded that surface area controls hydrogen adsorption and nitrogen content is not a relevant parameter.

1. Introduction

The US Department of Energy (DOE) set three goals for hydrogen storage systems to be used for automotive applications, which are reversibility, gravimetric density around 6 wt.% [1], and heat of adsorption (ΔH_{ads}) within the 20 – 30 kJ/mole range [2-3]. High surface area activated carbons (ACs) with optimal pore sizes around 0.5 – 0.7 nm have been suggested [4-6] as potential candidates to reach high hydrogen storage capacities at 77K. If high surface area is indeed necessary, it is not the only requirement and we have shown that an appropriate pore size distribution is also needed. Thus, H_2 uptakes higher than 3 wt. % at 77K are due to pores having diameters wider than 0.7 nm [7-8] in ACs prepared from KOH activation. Even if surface area and pore size distribution were optimised, we have experimentally shown that a maximum of hydrogen adsorption on ACs exists [9], and this maximum is very close to the 6.6 wt. % calculated by Schlappbach and Züttel [10].

The typical energy contribution from dispersive forces to hydrogen adsorption in porous solids such as ACs is roughly 6 kJ/mole, and remains well below the lower limit for the ideal ΔH_{ads} range (20 – 30 kJ/mole). A possible strategy for increasing the strength of the gas-solid interaction, and hence the hydrogen storage capacity of ACs, is the introduction of metal nanoparticles or heteroatoms in the carbon matrix [11]. Thus, doping ACs with Pd nanoparticles was tested as a method for improving hydrogen storage by spillover [12-16]. However, as hydrogen storage on high surface area-ACs at 77 K primarily depends on microporosity, Pd doping may decrease the micropore volume available for adsorption and hence the hydrogen storage capacities

[17].

Introduction of heteroelements significantly alters the electronic structure of the carbon matrix, thus affects the interactions between solid carbon and adsorbed hydrogen and might increase the amount of hydrogen stored. Promising results were obtained by introducing boron [18], silicon [19], sulphur [20] or nitrogen [21] into carbon. Nitrogen doping has been studied more extensively than the other heteroatoms, but contradictory results were reported in the literature. Zhou et al. [22] studied, through density functional theory (DFT) calculations, the effect of N-doping on hydrogen adsorption on single-walled carbon nanotubes. They found that N-doping decreased the hydrogen molecular adsorption energies. Kang et al. [23] found that hydrogen adsorption at 77K was more strongly related to specific surface area than to nitrogen content. Xia et al. [24] found that N-doping can be beneficial at low hydrogen uptake but is detrimental at high hydrogen uptake. Wang et al. [25-26] prepared nitrogen-doped ACs and found that hydrogen storage in such samples was much higher than that of non-doped materials of similar surface area. Finally, other studies concluded that nitrogen doping has no impact on hydrogen storage [27-29].

Therefore, the effect of nitrogen doping on hydrogen storage is still debated and, most of times, it is difficult to separate the combined effects of porosity and chemical composition. In the present manuscript, we doped three high surface area ACs, resulting in materials with nitrogen contents as high as 15.1 wt.%. Hydrogen storage capacity of raw and N-doped ACs was measured at 77K, and our results were compared to those reported in the open literature.

2. Experimental

2.1 Materials synthesis

The ACs' precursor was Chinese anthracite from Taisi mine, with an average particle size within the range 100 ~ 200 μm . ACs were prepared by chemical activation with KOH, as described elsewhere [9,30]. Nitrogen doping was then carried out by physical mixing of urea and AC, using urea to AC weight ratios of either 1 or 2, followed by thermal treatment in a horizontal furnace under air flowing at 50 cm^3/min . Temperature was increased at 5 K/min up to 623 K, the final temperature was maintained for 3 h, then the furnace was allowed to cool down to room temperature under air flow. The N-doped ACs were finally washed with hot water until neutral pH in a Soxhlet extractor, and dried.

2.2 Physicochemical characterization

2.1.1 Nitrogen content determination

Nitrogen content was determined by elemental analysis (EA) and X-ray photoelectron spectroscopy (XPS). EA was carried out in a ThermoFlash 1112 apparatus to determine carbon, hydrogen, nitrogen and sulphur contents. Oxygen content was obtained by difference. XPS spectra were recorded with an ESCAPlus OMICROM system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 10 kV and 15 mA under vacuum ($< 7 \times 10^{-7}$ Pa), using a non-monochromatised Mg $K\alpha$ X-Ray Source ($h\nu = 1253.6$ eV). Analyzer pass energies of 50 and 20 eV were used for full and detailed scans, respectively. The C1s

peak at 284.5 eV was used for binding energy correction.

2.1.2 Nitrogen physisorption

Nitrogen adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 automatic apparatus. The samples were degassed for 48h under vacuum at 523K prior to any adsorption experiment. Nitrogen adsorption data were obtained and treated as described elsewhere [9,30] for obtaining: (i) apparent surface area, S_{BET} , by the BET calculation method [31]; (ii) micropore volume, V_{DR} , according to the Dubinin-Radushkevich (DR) method [32 and refs. therein]; (iii) total pore volume, $V_{0.99}$, defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $P/P_0 = 0.99$ [33]. The mesopore volume, V_{me} , was calculated as the difference $V_{0.99} - V_{\text{DR}}$. The average micropore diameter, L_0 , and adsorption energy, E_a , were also calculated [34], as well as the pore size distributions (PSD) by application of the Density Functional Theory (DFT) [35].

2.1.3 Hydrogen storage

Adsorbed hydrogen uptake at 77 K was measured with a gravimetric analyzer (VTI Corporation). Hydrogen isotherms were obtained by setting pressure steps within the range 0 – 8 MPa at 77 and 298 K. More details are given elsewhere [9,30]. The counterpart excess hydrogen isotherms were measured in a volumetric device (HPVA-II, Micromeritics) in the same conditions.

3. Results and discussion

3.1 Materials composition

3.1.1 Elemental analysis

All ACs, non-doped and N-doped, were labelled AC_{xx}'y. In such nomenclature, x and x' correspond to the first two digits of the value of S_{BET} for the non-doped AC (N-doped AC precursor), whereas y is the weight ratio of urea to AC: 0 for non-doped ACs, and either 1 or 2 for N-doped ACs. For example, AC250 is a raw AC having a S_{BET} of 2500 m²/g, whereas AC251 is the N-doped counterpart prepared from AC250 using an urea/AC weight ratio (W) of 1.

Table 1 shows the results of elemental analysis of all studied ACs. Nitrogen content of raw materials was very low, typically ranging from 0.2 to 0.3 wt.%, whereas that of N-doped ACs was between 7.8 and 15.1 wt.%. Materials prepared from ACs having S_{BET} of 2527, 2955 and 3434 m²/g with W = 1 had nitrogen contents of 7.8, 9.9 and 8.8 wt.%, respectively. Using W = 2 in the AC30y series, the N content increased from 9.9 to 15.1% and C content decreased from 85.3 to 80.2%, whereas H and O contents remained roughly constant. These results seem to indicate that the amount of nitrogen in the final product not only depends on the oxygen content of the precursor, as concluded by Pietrzak et al. [36], but also on the value of W. As a result of N-doping treatment in the AC30y series, C/N ratio decreased dramatically and C/O ratio moderately increased (from 460.5 to 5.3 and from 12.6 to 20.2, respectively), essentially due to the decrease of C content.

3.1.2 XPS studies

Figure 1 presents full XPS spectra of N-doped samples. The region corresponding to N1s was carefully studied in order to follow some changes of bonding nitrogen to the carbon structure, as shown in Figure 2, in which the N1s bands were fitted for deconvolution with CASA software. The resultant contributions to N1s peaks are shown in Table 2.

N1s spectra of N-doped ACs were quite similar, all exhibiting an asymmetric, broad, band, whose deconvolution led to 3 contributions (Table 2) associated to different N functionalities according to the literature [37-48]. The first one at 398.1 – 398.2 eV can be assigned to pyridinic N (N-6), and the second one at 399.4 – 399.6 eV can be assigned to neutral amine (from model compounds reviewed in [48]). The last band ranged from 401.4 to 402.4 eV and, because of its width, could not be unambiguously assigned to only one type of N functionality. However, N-Q type with a low contribution of protonated amines seems to be the most reliable assignation. Therefore, the major contribution to N1s band, ranging from 54 to 73%, was that corresponding to amines. The nitrogen content of ACs before N-doping was so low that accurate N-contribution determination was impossible.

Table 2 also shows the contributions to C1s peaks. C1s bands (details not shown) were fitted by two and three peaks for raw and N-doped ACs, respectively. The first peak at 284.8 eV is associated to hydrocarbons (aliphatic and aromatics). The second one is related to both C-O single bond (ether, phenol) and to C associated with N. Such peak appeared at 285.5 eV for raw ACs, being primarily due to aliphatic

aliphatic carbons, and at 286.5 eV in N-doped ACs, being due to alcohols, phenols, C-N, carbons in keto-enolic equilibria and C-NO₂. The third peak, at 288.4 eV, is related to C=O in carbonyl and quinone, and to C associated with N. For AC302, such peak appeared at 287.4 instead of at 288.4 eV, due to the existence of keto-groups. The area of the first peak increased with the surface area, having a contribution of 32, 46.6 and 51.4 % for AC250, AC300 and AC340, respectively. Therefore, further activation produced more aliphatic and aromatic hydrocarbons and less C-O carbons. After N-doping, less aliphatic and aromatic hydrocarbons were observed, but the areas of the second and third peaks increased, due to the increased contribution of C-N groups.

The chemical compositions determined by EA on one hand, and by XPS on the other hand, are somewhat different. Comparison of Tables 1 and 2 indeed shows that the nitrogen contents are systematically lower at the surface of the materials than in the bulk. These findings are still unclear given that, in contrast, C/N and C/O ratios measured by both techniques are rather similar in non-doped materials.

3.2 Porous texture

Table 3 shows textural parameters determined by N₂ adsorption at 77 K for the 7 ACs considered in this study. All the ACs had apparent surface areas higher than 2000 m²/g, i.e. between 2082 and 3434 m²/g. They were mainly microporous since their micropore fraction, $V_{DR}/V_{0.99}$, ranged from 0.63 to 0.82. After nitrogen doping, a decrease of surface area and pore volume, both in the micro- and in the mesopore range, was observed. Weight ratios urea/AC of 1 and 2 decreased by 15-20% and by

30% the original surface area of the ACs, respectively. This finding is in agreement with the results of Pietrzag et al. [36].

Figure 3 a) shows the N₂ adsorption-desorption isotherms at 77K of the AC30y series before (AC300) and after N-doping with W = 1 (AC301) and W = 2 (AC302). Nitrogen isotherms were type I according to IUPAC classification, characterizing microporous adsorbents. N-doping treatment with urea did not affect the isotherm shape but all pore volumes, irrespective to the pore width. Figure 3 b) shows the PSD of the same AC series, confirming the conclusion derived from nitrogen isotherms. A clear decrease of all kinds of pore volumes was indeed observed when W was increased. Different from KOH activation, which has been thoroughly studied and activation mechanisms well explained [8,49,50], urea treatment effect on surface area is still under discussion. Pietrzag et al. [36] observed that urea treatment produced a surface increase on coals carbonized at 773 K but a surface decrease on coals carbonized at 973 K. They proposed that urea acts removing amorphous carbon blocking pores as well as creating new micropores and this effect was particularly important at low temperature. When urea treatment was applied to ACs prepared by KOH activation, it always produced surface area reduction [36]. Reduction of surface area when activated carbons were submitted to urea treatment was also found by other authors [51,52]. Arenillas et al. [51] suggested that the incorporation of nitrogen species to the edges of grapheme layers may create steric hindrances and partially block the access of nitrogen to pores.

Figure 4 shows the effect of nitrogen content determined by elemental analysis,

N-EA (%), on the values of S_{BET} for the 3 AC series. Changes of S_{BET} versus N-EA, just like those of V_{DR} (not shown), evidenced a nearly linear decrease. The discontinuous line is only a guide for the eye, and it can indeed be easily observed that we might also have drawn up three parallel lines corresponding to the 3 AC series.

3.3 Hydrogen storage capacity

Figure 5 a) shows hydrogen adsorption-desorption isotherms of the AC30y series at 77 K and up to 8 MPa. All the isotherms were type I, and a plateau was reached at 4 MPa. Hydrogen adsorption was completely reversible with high adsorption/desorption kinetics. Hydrogen adsorption was lower after nitrogen doping due to the decrease of S_{BET} , as demonstrated above, so that hydrogen adsorption capacity decreased in the order $\text{AC300} > \text{AC301} > \text{AC302}$. The same behaviour was observed in the other AC series.

Figure 5 b) presents the hydrogen adsorption capacities of the AC30y series as a function of N content. ACs before doping showed outstanding capacities of 5.4, 6.0 and 6.5 wt.% at 77K due to their high S_{BET} , 2527, 2955 and 3434 m^2/g , respectively. N-doped ACs had adsorbed hydrogen uptakes within the range 4.4 – 5.4 wt.%, i.e. always lower than those of their precursors. Therefore, N-doping appears to have a negative effect on the hydrogen storage capacity at 77K for the 3 AC series. Indeed, as explained above and as evidenced in Figure 4, the introduction of nitrogen into carbon by urea treatment produced a decrease of S_{BET} .

Excess hydrogen uptake, H_2 excess, is commonly reported and represents the amount of gas which is adsorbed additionally to the gas that would be present in the pore if there was no adsorption. For this reason, Figure 6 shows hydrogen excess uptake as a function of S_{BET} for 36 non-doped Taisi ACs [7-9, 30, 50] and the 7ACs reported in this study. Differences in H_2 excess are within the experimental error interval and, from this figure, it might be concluded that S_{BET} controls hydrogen storage at 77 K while nitrogen content has no effect. In order to confirm that, we will compare our results to those obtained in former studies in the next section.

3.4 Effect of nitrogen content, comparison with other literature data

Most of hydrogen storage capacities reported in the open literature were measured at a lower pressure than for our own data, i.e. at 2 MPa instead of 4 MPa [23, 24, 28, 29]. Figure 7 a) and b) shows H_2 excess uptake at 2MPa as a function of S_{BET} and nitrogen content for the aforementioned references and our data. In these former studies, nitrogen content was determined by XPS [24, 29] (Figure 7 a) or EA [23, 24, 28] (Figure 7 b). XPS gives nitrogen content at the surface of the materials, whereas EA gives nitrogen content in the bulk. These two kinds of measurement give results that are sometimes quite different. Therefore, nitrogen contents determined by XPS and by EA were treated separately. H_2 excess is clearly dependent on S_{BET} but it is difficult to see the effect of nitrogen content, especially in Figure 7a). For this reason, we applied the analysis of variance (ANOVA) not only to results reported in literature but also to our results. ANOVA is a method of partitioning variability into

identifiable sources of variation and the associated degrees of freedom in an experiment. The ANOVA was done at 95% confidence level (α level), based on the sum of the squares (SS), the degree of freedom (df), the mean square, and F and P values. Usually, the larger the F value, the greater the effect of an experimental variable on the results [53]. Table 4 shows the results of ANOVA for a linear model where H_2 excess would be a function of S_{BET} and N content, determined by XPS or EA. The highest F values were obtained for S_{BET} , thus confirming that S_{BET} has the most important effect on hydrogen storage. The last column gives P values. If a P value is less than, or equal to, α level (0.05 in this case), then the variable has no significant effect. We can observe that only N content has a P value higher than 0.05: 0.149 (for N determined by XPS) and 0.063 (for N determined by EA). Therefore, we can conclude that nitrogen content has no significant effect on hydrogen storage at 77 K.

Figure 8 shows excess H_2 uptake as a function of S_{BET} for the data reported in the literature [23, 24, 28, 29] and data obtained this study. H_2 excess is linearly dependent on S_{BET} up to $2630 \text{ m}^2/\text{g}$, which is the theoretical maximum surface of carbon [9, 10, 50], and this is in agreement with the ANOVA analysis.

4 Conclusions

Urea treatment at 623K under air flow allowed synthesising ACs with nitrogen contents as high as 15.1 wt.%. However, apparent surface areas and pore volumes were considerably decreased, and hence hydrogen storage capacities were lower after N-doping.

Statistical analysis, ANOVA, of the relevancy of S_{BET} and nitrogen content on hydrogen storage at 77 K was carried out, taking into account our data and those data available in the open literature. An ANOVA analysis was done for samples analysed by EA and a second one for samples analysed by XPS. Both ANOVA analyses showed that: (i) S_{BET} controls hydrogen adsorption, and (ii) nitrogen content is not a relevant parameter.

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Captions of the Figures

Figure 1. XPS survey for N-doped samples.

Figure 2. Experimental XPS N1s spectra of N-doped samples and corresponding deconvolution of the fit (colour online).

Figure 3. Effect of W: a) on the N₂ adsorption - desorption (full and empty symbols, respectively) isotherms at 77 K, and b) on the pore-size distribution of the AC30y series (♦ AC300, ▲ AC301 and ● AC302).

Figure 4. Changes of S_{BET} with N content determined by EA (● AC25y series, ♦ AC30y series and ▲ AC35y series)

Figure 5. a) Hydrogen adsorption isotherms at 77K of the AC30y series; b) Changes of hydrogen adsorption with N-content determined by EA.

Figure 6. H₂ excess uptakes at 77 K and 4 MPa as a function of S_{BET} for 36 non-doped (■) and this study (□) ACs, all of them derived from Taisi anthracite.

Figure 7. H₂ excess uptakes at 77 K and 2 MPa as a function of S_{BET} and nitrogen content determined by a) XPS and b) EA (♦ [23], ● [24], ◆ [28], ○ [29], □ our data).

Figure 8. H₂ excess uptakes at 77 K and 2 MPa as a function of S_{BET} (same symbols as in Figure 7).

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Table 1. Elemental analysis (EA) of all ACs, and corresponding C/N and C/O weight ratios.

Sample	EA (wt.%)					C/N	C/O
	C	H	N	S	O		
AC250	92.96	0.42	0.31	0.00	6.31	299.87	14.73
AC251	84.63	2.63	7.83	0.00	4.91	10.81	17.23
AC300	92.10	0.36	0.20	0.00	7.34	460.50	12.55
AC301	85.28	0.54	9.90	0.00	4.28	8.61	19.92
AC302	80.23	0.72	15.07	0.00	3.98	5.32	20.16
AC340	93.95	0.32	0.24	0.00	5.49	391.46	17.11
AC 341	86.56	0.47	8.78	0.47	3.72	9.86	23.27

*Determined by difference

Table 2

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Table 2. Contributions to N1s and C1s bands in XPS patterns in terms of binding energy (BE, eV) and area of the peak (%), and corresponding surface compositions (wt.%).

Sample	BE (eV) and area of the peak (%)						(wt.%)				
	N1s peak			C1s peak			C	N	O	C/N	C/O
	Pyridinic (N-6)	Neutral amines	Quaternary-N (N-Q)	Hydrocarbons (aliphatic, aromatic)	C-O (ether, phenol) C associated with N	C=O (carbonyl, quinone) C associated with N					
AC250	398.3 (7)	400.7 (43)	401.9 (50)	284.4 (32.9)	285.6 (67.1)		91.7	0.3	8.0	305.7	11.5
AC251	398.2 (17)	399.6 (63)	402.4 (20)	284.4 (47.8)	286.4 (52.2)		89.1	5.1	5.8	17.5	15.4
AC300	398.2 (2)	400.8 (12)	401.9 (84.9)	284.4 (46.6)	285.4 (53.6)		89.5	0.2	10.3	447.5	8.7
AC301	398.2 (20)	399.6 (54)	401.4 (26)	284.4 (43.1)	286.6 (53.2)	288.8 (3.7)	84.4	5.4	10.2	15.6	7.6
AC302	398.1 (24)	399.4 (55)	401.8 (20)	284.4 (36.1)	286.7 (57.7)	287.4 (6.2)	83.9	7.1	9.0	11.8	9.3
AC340	n.d.	n.d.	n.d.	284.4 (51.4)	285.7 (48.6)		93.6	0.1	6.3	936.0	14.9
AC341	398.2 (7)	399.4 (73)	401.6 (20)	284.4 (41.1)	286.4 (52.7)	288.4 (6.1)	87.0	3.5	9.5	24.9	9.2

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Table 3 Textural parameters of all ACs.

	S_{BET}	$V_{0.99}$	V_{DR}	Ea	Lo	$V_{\text{DR}}/V_{0.99}$	V_{me}
samples	(m^2/g)	(cm^3/g)	(cm^3/g)	(kJ/mol)	(nm)		(cm^3/g)
AC250	2527	1.10	0.90	22.1	1.0	0.82	0.19
AC251	2082	0.89	0.72	23.0	0.9	0.81	0.17
AC300	2955	1.39	1.01	20.3	1.2	0.73	0.38
AC301	2541	1.12	0.82	21.4	1.1	0.74	0.29
AC302	2160	0.96	0.70	21.8	1.0	0.73	0.26
AC340	3434	1.61	1.02	19.3	1.4	0.63	0.59
AC341	2737	1.29	0.84	20.5	1.2	0.65	0.45

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Table 4 ANOVA parameters for [23, 24, 28, 29] and our data

	<i>SS</i>	<i>df</i>	<i>F</i>	<i>P</i>
N determined by XPS (Figure 7a)				
S_{BET}	117.664	1	771.670	0.000
N	0.350	1	2.294	0.149
Error	2.440	16		
Total	407.331	18		
N determined by EA (Figure 7b)				
S_{BET}	226.104	1	2173.152	0.000
N	0.397	1	3.819	0.063
Error	2.393	23		
Total	359.887	25		

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Figure 1

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Figure 2

Figure 3

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Figure 3

a)

b)

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Figure 4

Figure 5

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Figure 5

a)

b)

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Figure 6

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Figure 7

a)

b)

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Figure 8

Supplementary Material

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