Catalysis Today 65 (2001) 129–135

www.elsevier.com/locate/cattod

Linear hexane isomerization over the natural zeolite based catalysts depending on the zeolite phase composition

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Abstract

A range of Pd-containing catalysts on the basis of mordenite–clinoptilolite rocks of different starting phase compositions is synthesized. Final phase composition and acidity of rocks change as the conditions of their dealumination are changed. The efficiency of catalysts synthesized is weakly influenced by change of mordenite component contents within 50–80%, and it is not inferior to the efficiency of the catalysts on the synthetic mordenite basis. The nature of active sites as trifunction ones and isomerization mechanism are proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Natural zeolites; Mordenite–clinoptilolite composition; Modification; Acidity, activity, selectivity; Linear hexane isomerization; Mechanism; Active site nature

1. Introduction

Besides the studies of the isomerization catalysts on sulphated zirconia and acidified alumina basis, scale developments of isomerization catalysts on the basis of zeolites [1–12] are continued, the most common zeolite being the synthetic mordenite [1–3,5,8]. Earlier the optimum Si/Al ratio for the last was determined as being equal to 9 [13]. It is stated [5] that among the catalysts Pt/H-beta, Pt/HM, and Pt/HZSM-22 only the mordenite sample is characterized by the positive enthalpy of protonation.

The evaluation of the natural mordenites is of considerable interest since they have the advantage of cheapness and do not need any special stage of forming. It is shown [4,9] that catalysts based on the natural Ukrainian mordenites are comparable with the synthetic mordenite based ones.

Unfortunately, in contrast to the synthetic mordenite, the Ukrainian natural zeolite rocks are of 50–80% mordenite phase content only. The main satellite phase is the clinoptilolite. Among other admixtures the feldspar (to 5%) predominates. The most efficient catalysts were obtained on the acid treatment of the previously decationated rocks [4].

The study of the influence of the rock mordenite contents on the properties of the catalysts obtained under the optimum conditions of their modification is of great scientific and practical interest.

2. Experimental

Rocks A, B (Ukraine), and C (Georgia) were subjected to chemical and thermochemical modifica-

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PII: S0920-5861(00)00573-3

Table 1
Chemical compositions and micropore volumes (with respect to water) of the zeolite-containing rocks of some Ukrainian and Georgian deposits

Rock	Composition (wt.%)						Micropore volume (cm^3/g)	Si/Al
	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	H_2O		
A (Ukraine)	65.90	11.85	2.91	1.12	2.07	10.92	0.157	4.6
B (Ukraine)	64.95	12.23	3.22	0.70	2.35	12.33	0.164	4.5
C (Georgia)	63.90	11.95	4.09	0.95	0.76	14.07	0.148	4.4

tion. Mordenite/clinoptilolite ratios in rocks A and B amounted to 3:1 and 1:1, respectively. Rock C was on the whole a pure natural clinoptilolite. All rocks were of close chemical compositions and micropore volumes (Table 1).

The parent rocks and their H-forms (both as crumbs of 0.25–1 mm) were dealuminated either with 5 M HCl or 2.5 M H_2SO_4 (solid to liquid phase ratio 1:10) for 3 h at 373 K. The H-forms were obtained previously through the calcination of the NH_4-forms in air for 2 h at 873 K.

The composition, adsorption, and X-ray studies of parent rocks and their modified samples were carried out as already described [4], the acidity of the modified rocks was investigated by the temperature programmed desorption (TPD) of ammonia according to Patrylak [14]. Palladium (0.5 wt.%) was supported on the specimens modified, the catalysts obtained were tested, and the reaction products analysed in accordance with [4].

3. Results

The data listed in Table 2 show that under the same conditions of the treatment of the parent rocks the samples obtained are of greatly different final Si/Al ratio values. The last depend not on the form of the rock treated only (parent or decationized), but on the acid nature too, as is seen from the powder X-ray diffraction spectra of differently treated samples of the rock B (Fig. 1). So, the previous decationization of the rock provides the more high degree of safety of the clinoptilolite phase during the dealumination procedure by both acids on the whole, though the sulphuric acid seems to be more endurable for this phase.

The accessibility of the micropores for the *n*-hexane and benzene molecules (the last are close to isohexane molecules in their kinetic diameter of 0.585 nm [15]) is greater in the case of modified rock A.

In Fig. 2 TPD spectra of parent rocks as well as of all samples listed in Table 2 are depicted. One of the

Table 2
Influence of the acid treatment of the mordenite–clinoptilolite rocks on their Si/Al ratios and micropore volumes

Sample number	Preparation method		Si/Al	Micropore volume (cm^3/g)	
	Parent sample	Acid		C_6H_6	C_6H_{14}
1	Rock A	HCl	10.2	0.087	0.090
2	Rock A	H_2SO_4	8.4	0.076	0.086
3	H-form of rock A	HCl	7.6	0.058	0.077
4	H-form of rock A	H_2SO_4	7.2	0.047	0.072
5	Rock B	HCl	11.5	0.059	0.077
6	Rock B	H_2SO_4	9.3	0.068	0.077
7	H-form of rock B	HCl	5.6	0.054	0.063
8	H-form of rock B	H_2SO_4	5.4	0.046	0.067
9	Rock C	HCl	37.2	0.070	0.072
10	Rock C	H_2SO_4	11.2	0.077	0.080

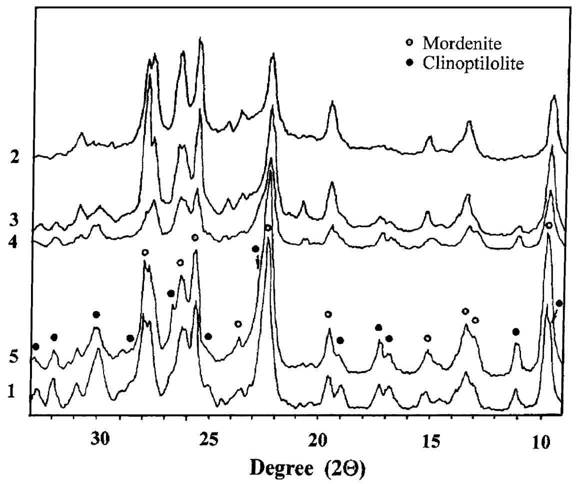


Fig. 1. X-ray diffraction evidences of the rock B which has been not subjected to the acid treatment (dealumination) and of one dealuminated under various conditions: (1) parent, do not subjected to the dealumination; (2) parent, HCl (sample 5); (3) parent, H_2SO_4 (sample 6); (4) H-form, HCl (sample 7); (5) H-form, H_2SO_4 (sample 8).

known shortcomings of the TPD is that this method does not strictly discriminate the physical adsorption of ammonia in zeolite micropores from its chemisorption on the acid sites. This shortcoming is especially expressed for the narrow-porous zeolites, first of all — clinoptilolite. Just the great physical adsorption of ammonia gives rise to the TPD spectra of the parent rocks (Fig. 2a), the spectrum of A being noticeably inferior to the spectrum of B in area but the same in character.

The spectra of rocks modified are characterized by the trend towards increase of the contribution of the high-temperature desorption into the total amount of ammonia desorbed, which, undoubtedly, is due to the additional strong acid sites. The hydrochloric acid treatment of all parent rocks results in the high-temperature ammonia desorption increase especially significantly (Fig. 2b), while the sulphuric acid acts, on the whole, considerably less, increasing the high-temperature ammonia desorption for A and C greater than for B (Fig. 2c). The most similar ammonia TPD spectra of more intensive high-temperature peaks were obtained for the dealuminated H-form samples of A, the spectrum of H_2SO_4 treated sample being greater in area (Fig. 2d and e). In contrast, for the acid treated H-form samples of B, TPD spectra of near areas and sloping appear, but of rather more intensive low-temperature peaks (Fig. 2d and e).

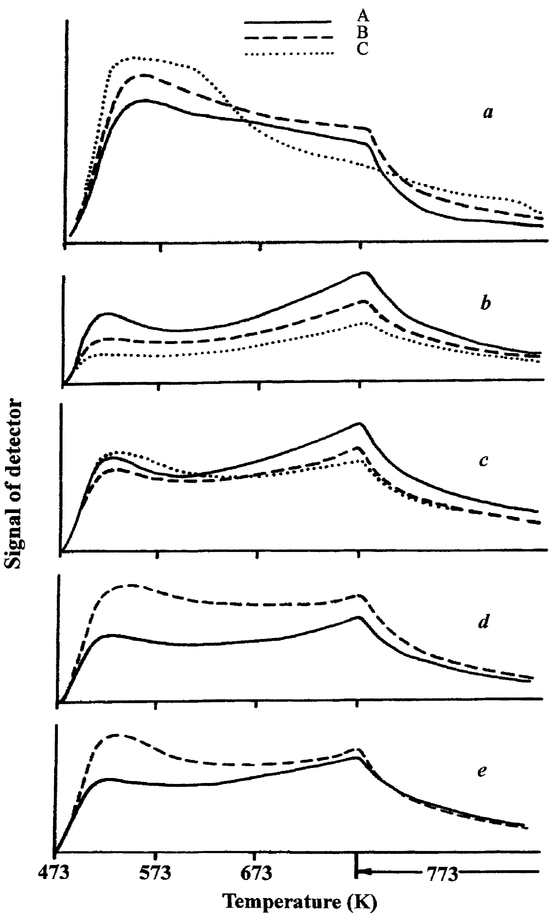


Fig. 2. TPD spectra of samples of modified rocks, grouped according to the mode of modification: (a) parent rocks A–C; (b) parent rocks A–C treated by hydrochloric acid; (c) parent rocks A–C treated by sulphuric acid; (d) H-forms of rocks A and B treated by hydrochloric acid; (e) H-forms of rocks A and B treated by sulphuric acid.

The described peculiarities of TPD spectra, the chemical composition of samples and their X-ray data (Fig. 1) allow to conclude that a part of sites, which have the greatest adsorption energy for ammonia ($T \geq 773$ K peak), increases as Si/Al ratio increases and clinoptilolite contents decrease. Last values vary not only depending on the phase composition of parent rocks, but on their modifying conditions too.

Table 3
Hydroisomerization of linear hexane

Sample number	T (K)	Conversion (%)	Selectivity (wt.%)										$\frac{2,2\text{-DMB}}{\Sigma i\text{-C}_6}$(wt.%)
			C_1–C_3	i-C_4	n-C_4	i-C_5	n-C_5	ΣC_4–C_5	2-MP	3-MP	2,2-DMB	Σi-C_6	
1	573	76.7	2.5	2.6	2.4	4.2	2.1	11.3	45.9	25.5	14.8	86.2	17.2
	548	64.1	0.5	0.3	0.5	0.7	0.5	2.0	54.5	30.6	12.4	97.5	12.7
	523	35.2	0.1	0.1	0.1	0.2	0.5	0.9	59.2	32.1	7.7	99.0	7.8
2	573	56.7	2.0	1.6	1.4	2.9	1.6	7.5	51.6	28.9	10.0	90.5	11.0
	548	35.8	0.5	0.3	0.5	0.6	1.3	2.7	56.8	32.9	7.1	96.8	7.3
	523	13.9	0.2	0.4	0.6	1.2	2.4	4.6	55.4	31.9	7.9	95.2	8.3
3	573	73.7	0.5	0.7	0.9	1.9	1.1	4.6	47.0	34.1	13.8	94.9	14.5
4	573	78.5	0.4	2.7	1.6	6.9	3.0	14.2	43.7	27.6	14.1	85.4	16.5
5	573	72.0	0.4	0.8	0.5	2.0	0.8	4.1	49.7	36.8	9.0	95.5	9.4
6	573	71.8	0.2	0.8	0.7	3.8	1.8	7.1	46.0	37.3	9.4	92.7	10.1
7	573	79.5	1.1	2.6	1.5	4.4	1.6	10.1	46.5	26.1	16.2	88.8	18.2
	548	68.8	0.4	0.4	0.5	0.9	0.5	2.3	55.4	29.0	12.9	97.3	13.3
	523	37.5	–	–	–	Traces	Traces	Traces	61.7	29.7	8.6	100.0	8.6
8	573	77.1	0.4	2.7	2.4	6.7	2.9	14.7	43.7	28.6	12.6	84.9	14.8
9	573	52.8	0.4	0.2	0.3	0.4	0.6	1.5	56.9	31.9	9.3	98.1	9.5
	548	28.1	–	–	–	0.1	Traces	0.1	59.9	34.6	5.5	99.9	5.5
	523	12.2	0.1	0.1	0.1	0.6	0.4	1.2	56.8	35.7	6.2	98.7	6.3
10	573	18.2	0.2	0.2	0.8	0.3	0.8	2.1	58.6	36.2	2.9	97.7	3.0
	548	4.8	–	–	0.2	0.2	0.8	1.2	56.7	40.6	1.5	98.8	1.5
	523	1.7	–	–	–	0.3	0.9	1.2	63.5	34.7	0.6	98.8	0.6

In general, acidity data (Fig. 2b–e) confirm the conclusions drawn from the X-ray measurements (Fig. 1) concerning the clinoptilolite phase stability under different conditions.

In Table 3 the testing results for 573, 548, and 523 K are presented. The best part of samples is notable for high activity and selectivity, the latter being decreased in following order: 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB). The amounts of C_1–C_5 hydrocarbons do not exceed 15% on the converted hexane, C_1–C_3 contents of C_1–C_5 being not great ones. C_7 hydrocarbons are found as traces only. It is strange, but no 2,3-dimethylbutane (2,3-DMB) was found in reaction products.

On the whole, at testing temperature of 573 K the samples on the basis of A and B are close to each other: except sample 2, obtained by treatment of parent rock A with the sulphuric acid, they are characterized by the hexane conversion above 70 wt.% and by selectivity of 85–95 wt.% for total i-C_6 on n-C_6 converted amount. The selectivity for 2,2-DMB is fluctuating from 9.4 to 18.2 wt.%. The samples on the basis of C are strongly inferior to the previous catalysts, especially being distinguished sample 10 — the product of the sulphuric acid treatment.

The samples 1, 5, 9 on the basis of HCl treated parent rocks are all in all somewhat superior in their efficiency to the analogous samples 2, 6, 10 obtained with the use of H_2SO_4 which, most likely, is due to the greater strong acid site contents of HCl treated rocks (Fig. 2). Considerably lower isomerization data on samples 2 and 10, are possibly caused by their high strong acid site contents in the narrow eight-ring channels of clinoptilolite which are not accessible even for linear hexane molecules (Table 3 and Fig. 1).

The dealumination of the previously decationized A and B leads to the high efficient catalysts independently on the nature of the acid: samples 3, 4 and 7, 8, the most effective of which are 4 and 7 ones, were obtained on the basis of different rocks using different acids.

The decrease of the testing temperature to 548 and 523 K results (Table 3) in a considerable decrease in the linear hexane conversion and in a noticeable, on the whole, selectivity increase for total i-C_6, but in the simultaneous selectivity decrease for 2,2-DMB. The sample 10 is characterized by the lowermost selectivity for this isomer at all testing temperatures.

4. Discussion

The data for samples 1, 3, 4, 7, and 8 given in Table 3 are comparable with the new isomerization data for catalysts on the basis of synthetic mordenite. So, over Pt/HM [16] at 270 and 280°C linear hexane conversions of 70.9 and 74.3%, total isohexane yields of 69.5 and 70.8%, and selectivities (on linear hexane converted) for isohexanes of 98.3 and 95.3%, respectively, were attained, while the 2,2- and 2,3-DMB total contents of isomerizate made 13.9 and 15.0%, respectively.

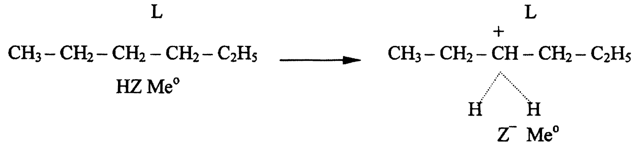
The determinant of the efficiency of the samples obtained, of course, is spectrum of their acidity, first of all that of the mordenite phase. Unfortunately, the biphaseness of A and B gives one no chance to follow separately the properties of the mordenite phase of samples concerning the Si/Al value and the acid spectrum character. A very significant fact, however, is that the acid treated H-forms of A and B give high-efficient samples 3, 4, 7 and 8 practically independently on phase composition of rocks and nature of acid used, the TPD spectra in pairs 3, 4 and 7, 8 being very similar, but very different for each pair (Fig. 2d and e). The high efficiency of samples 3 and 4 may consist in the heightened mordenite phase contents and in the predominance of the strong acid sites. But the mordenite phase of parent rocks not as a whole performs the role of active phase, therefore the change of mordenite content of rocks within 50–80% is not of decisive significance. As for samples 7 and 8, the character of their TPD spectra surely is due to the considerable clinoptilolite contents. Nevertheless, we do not think that the clinoptilolite component increases the isomerization efficiency of catalysts in itself. Most likely, the positive effect is due to the heightened capability of the mordenite component of B to dealumination displacing of the part of framework aluminium atoms into the extra-framework positions [17] which results in the attainment of the optimum Si/Al ratio of mordenite phase. Mordenite and clinoptilolite components are genetically interlinked as well as intermixed extremely delicately, and the atoms of the extra-framework, coordinatively unsaturated aluminium, which emerged upon the destruction of the clinoptilolite phase during the procedures of the rock modifications, may be distributed among Broensted acid sites of mordenite phase also in an extremely delicate manner. Additionally, the palladium atoms introduced into the samples by the ion exchange technique may be distributed to such a degree of perfection too. These circumstances are able to cause the formation of the unique isomerization active sites which include Broensted and Lewis sites as joined together with the dehydrogenation–hydrogenation sites.

Bolton and Lanewala [18] arrive at a conclusion that the bimolecular hexane isomerization mechanism over Pt/HY through the formation of intermediates of cyclohexane series is realized. A scheme of hexane isomerization on the amorphous catalyst, acidified alumina supported platinum [19], is proposed. The last postulates the formation of all hexane isomers from the primary 2-MP, those isomers in themselves being more limited in their conversions.

Do not excluding the possibility of realization of various mechanisms over various catalysts, we incline, however, to monomolecular mechanism: the narrowness of the mordenite (and clinoptilolite) micropores scarcely gives grounds for the consideration of the bimolecular mechanism as well as for the presumption that the intermediates and the final products of a great molecular weight would be formed as it can occur over the catalysts on the basis of the wide-pores zeolites [18] or alumina [19].

Below it is presented the isomerization mechanism which includes the intramolecular hydride and carbanion transfers, the last — obeying the rule of β-scission.

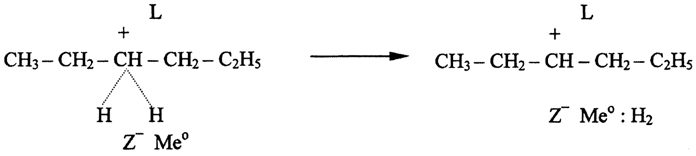
Assume the third C atom of linear hexane molecule to be protonated leading to the appropriate non-classical carbonium ion:



$$\underset{\mathrm{HZ\,Me^{o}}}{\overset{\mathrm{L}}{CH_3-CH_2-CH_2-CH_2-C_2H_5}} \longrightarrow CH_3-CH_2-\overset{\overset{\mathrm{L}}{+}}{\underset{\underset{Z^-\,Me^{o}}{H\;\;\;H}}{CH}}-CH_2-C_2H_5$$

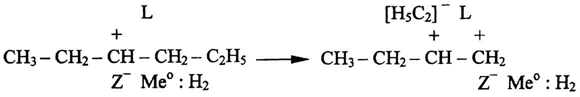
where by HZ, Me^0, and L Broensted site, palladium or platinum in null valence state, and Lewis site are denoted, respectively.

Then Me^0 abstracts two hydrogen atoms from the carbenium ion transforming the last to the classical carbenium ion [4]:



$$CH_3-CH_2-\overset{+\ \ \mathrm{L}}{\underset{\underset{Z^-\,Me^{o}}{H\;\;\;H}}{CH}}-CH_2-C_2H_5 \longrightarrow \underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{+\ \ \mathrm{L}}{CH}-CH_2-C_2H_5}$$

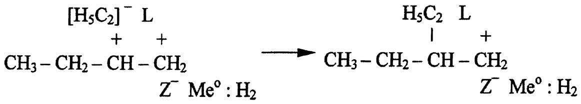
According to the β-scission rule, this classical carbonium ion may decay, splitting off either CH_3 or C_2H_5 groups, most likely, as carbanions, thanks to neighbourhood of positive charge and Lewis site



$$\underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{+\ \ \mathrm{L}}{CH}-CH_2-C_2H_5} \longrightarrow \underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{[H_5C_2]^-}{\overset{+}{CH}}-\overset{\mathrm{L}}{\overset{+}{CH_2}}}$$

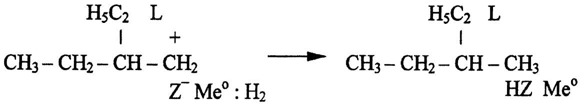
the positive charge at the emerged primary C atom being stabilized by the negatively charged zeolite site [20].

The following step leads towards the branched carbocation:



$$\underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{[H_5C_2]^-}{\overset{+}{CH}}-\overset{\mathrm{L}}{\overset{+}{CH_2}}} \longrightarrow \underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{H_5C_2}{\overset{|}{CH}}-\overset{\mathrm{L}}{\overset{+}{CH_2}}}$$

Finally, palladium returns the hydrogen as hydride ion and proton [4] to the branched carbenium ion and to the catalyst, respectively, which results in the 3-MP molecule and catalyst active site restauration



$$\underset{Z^-\,Me^{o}:H_2}{CH_3-CH_2-\overset{H_5C_2}{\overset{|}{CH}}-\overset{\mathrm{L}}{\overset{+}{CH_2}}} \longrightarrow \underset{\mathrm{HZ\ Me^{o}}}{CH_3-CH_2-\overset{H_5C_2}{\overset{|}{CH}}-\overset{\mathrm{L}}{CH_3}}$$

Just so one can imagine the emergence of 2-MP as well as all of other isomerization products depending on the starting hexane molecule. Under such handling, the isomerization catalyst should be considered not as dual, but even as a trifunction one.

The distribution of the isomerization products under the conditions of real isolation of the converted molecules in micropores is controllable not only thermodynamically, but kinetically too. The mentioned absence of 2,3-DMB in reaction products as well as 3-MP/2-MP ratios lesser then unity (2,3-DMB and 3-MP seem to be the two most active isomers among all hexanes [4]) may be caused just by such a situation. Besides, approaches to the isomerization mechanism through the formation and transfer of carbanions CH_3^-, $C_2H_5^-$ and $C_3H_7^-$ do not exclude the possibility of hydride ions abstraction from such carbanions by the intermediate positive charge, following neutralization of the last by these hydride ions and simultaneous formation of ethylene and propylene from $C_2H_5^-$ and $C_3H_7^-$ as well as the emergence of radical $CH_2^{\bullet\bullet}$ from CH_3^- which can recombine with another such radical to the additional ethylene. The formed ethylene and propylene give rise to C_4–C_5 olefins which, being hydrogenized, are added to C_4–C_5 paraffins from the retained linear fragments of hexane on the active sites. Hence it follows the molar disproportion between the C_1–C_3 and C_4–C_5 in the reaction products in favour of C_4–C_5 (Table 3).

Thus, catalysts for isomerization on the basis of mordenite–clinoptilolite rocks have a number of peculiarities. The last are not always negative ones which affords the opportunity to obtain the high efficient samples.

5. Conclusion

The change of the ratio of the mordenite to clinoptilolite in parent Ukrainian rocks within 3:1–1:1 does not essentially affect the properties of the catalysts synthesized. The catalysts obtained are not inferior to the samples on the basis of the synthetic mordenite. But one failed to obtain the efficient isomerization catalysts on the basis of Georgia clinoptilolite rock. The hydrochloric acid exhibit some advantages as a dealuminating agent in comparison with the sulphuric acid. The isomerization mechanism as such one that is realized on the trifunction active sites is proposed.

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