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Coupled hydrogenation and ring opening of tetralin on potassium modified Pt/USY catalysts

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Coupled hydrogenation and ring opening of tetralin (THN) on Pt/USY catalyst were performed on a high-pressure fixed-bed reactor. The effect of reaction temperature in range of 100–300 °C and the nature of the catalyst (metal and acid sites) on the catalytic performance were studied. The results indicated that the extent of hydrocracking, a sequential reaction of ring opening, should be reduced in order to maintain high yields of the ring opening products (ROP). Introduction of the Pt component accelerated the hydrogenation and ring opening of the THN significantly. It was also found to be an effective way to optimize the acid properties of the catalysts by introducing an appropriate amount of potassium to the catalyst, such that the strong acid sites of the catalysts were diminished, and a higher ROP yield could be obtained as a result of the inhibiting of the hydrocracking activity of the catalyst. When the yield of the C10 fractions could be maintained at 90 wt.%, then a maximal ROP yield of 35.6 wt.% could be obtained on a 0.5 wt.% Pt/USY catalyst loaded with 2.0 wt.% of K.

KEY WORDS: tetralin; decalin; hydrogenation; ring opening; Pt/USY; diesel.

1. Introduction

Too high aromatic contents in diesel fuels have been recognized as detrimental both in lowering the fuel qualities and in contributing significantly to the formation of undesirable tailpipe emissions [1–3]. For the sake of environment protection, more stringent legislations associated with clean fuels have been made [2,4]. Key product requirements for diesel range distillates include an ultra-low-sulfur content and a low polynuclear aromatic concentration [5]. Therefore, the light cycle oils (LCO) of FCC containing 60–70 vol.% aromatics [6] cannot be used directly as accession for diesels. Accordingly, the removal of polynuclear aromatics and the enhancement of cetane numbers of diesel fuels become the focal point of intense researches [4–6].

Commercially, two technologies are being employed for improving diesel qualities by the removal of polynuclear aromatics, aromatic saturation (ASAT) and hydrocracking [1,2,5]. However, both of them have some limitations [5]. An interesting and alternative technology for improving the cetane number of diesels and maintaining meanwhile high diesel yields is achieved by combining a complete hydrogenation process with a selective ring opening (SRO) reaction of the naphthenic rings [7]. The SRO is defined as follows: naphthene rings are opened to form compounds with high cetane number, but without any carbon losses [5,8]. McVicker and co-workers have indicated that metal-catalyzed hydrogenolysis was a potential approach for achieving the SRO [5,9–12]. Meanwhile, five-membered-rings are much easier to be opened than their six-membered counterparts due to the higher ring strain energies of the former, i.e., 6–7 kcal/mol, as compared to the 1 kcal/mol of the latter [13]. In order to perform hydrogenation and ring opening of polynuclear aromatics, bifunctional catalysts containing both metal component(s) and acid sites have been employed in most cases [4–7,9–21].

More recent studies demonstrated that complete hydrotreating of the aromatics prior to ring opening was needed [22–24], and cis-decalin converts much more selectively to ring-opening products than trans-decalin [7]. Meanwhile, we noticed that complete hydrogenation of naphthalene could perform on noble-metal/zeolite catalysts even at low temperature [25], and high selectivity of cis-decalin could be obtained on Pt/Y compared with Pd/Y [26]. Thus, Pt/USY was used as catalyst in the present study, and potassium was introduced to tune the acid properties of the catalysts, as has been elucidated by Song *et al.* [27], so as to obtain high ROP yields and to restrict the products within the diesel range. As a partial hydrogenation product of naphthalene, THN

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was used as model reactant. The influence of reaction temperature was studied in wide temperature range. Then the active sites of the catalysts were also optimized by varying the loadings of Pt and K, so as to enhance the ROP yield and to restrain further the hydrocracking reactions.

2. Experimental

2.1. Catalyst preparation

H-USY zeolite was obtained from Petro Qilu, with bulk $SiO_2/Al_2O_3 = 4.8$. Catalyst supports with different K loadings (nominal content of 0.4, 1.2 and 2.0 wt.%) were prepared by incipient wetness impregnation of USY zeolites (20–40 mesh) with aqueous solutions of KNO_3 containing the required amounts of KNO_3, and denoted as 0.4 K-USY, 1.2 K-USY and 2.0 K-USY, respectively. After impregnating with K, the samples were maintained at ambient temperature overnight, then dried at 110 °C for 3 h, and finally calcined at 520 °C for 3 h. Then, 0.5 wt.% Pt was incorporated with a 0.1 mol/L HCl aqueous solution containing the required amount of hexachloroplatinic acid by using the same procedure as the impregnation of potassium. The as-prepared samples were denoted as 0.5 Pt/0.4 K-USY, 0.5 Pt/1.2 K-USY and 0.5 Pt/2.0 K-USY, respectively. For comparison, a catalyst having an identical Pt-loading but without K-loading was prepared, and denoted as 0.5 Pt/USY. Meanwhile, Pt/USY with different amounts of Pt were prepared to study the influence of Pt loading.

2.2. Catalyst characterization

Powder XRD patterns of the supports with different K-loadings as well as the USY were recorded on a PANalytical X'Pert PRO diffractometer using Cu K_α radiation ($\lambda = 1.5404$ Å) at 40 kV and 40 mA. Chemical compositions were determined with a Philips Magix X-ray fluorescence spectrometer. The BET surface areas and pore volumes were determined on a Micromeritics ASAP-2010 physical analyzer by N_2 adsorption at −196 °C.

Acidities of the supports were determined by temperature-programmed desorption (TPD) of adsorbed ammonia using the same procedure described in Ref. [28]. Brönsted (B) and Lewis (L) acid sites of the samples were determined by FT-IR spectroscopy of adsorbed pyridine. Room-temperature IR spectra were recorded on a Nicolet 710 FT-IR from zeolite wafers ($10 mg/cm^2$) mounted on a vacuum cell. Pretreatment of the samples was performed in the cell at 500 °C under vacuum for 2 h. For adsorption/desorption studies, pyridine vapor was adsorbed onto the sample, and the excess pyridine was removed under vacuum over two consecutive periods (1 h for each) under heating at 150 and 350 °C, respectively, then each of them was followed by IR measurements. The density of both types of acid sites was quantified by integrating the corresponding absorption bands and using the molar extinction coefficients obtained by Emeis [29].

2.3. Catalytic activity test

Hydrogenation and ring opening of THN were performed in a high-pressure fixed-bed stainless reactor (10.0 mm i.d. and 600 mm in length). The reaction temperature was controlled by two thermocouples placed at two fixed points of the upper and lower furnace, respectively, and the reactor temperature was measured with a thermocouple placed in the center of the catalyst bed. An organic feed consisting of a solution of THN in *n*-heptane (20.0 wt.%) was introduced by means of a micro-pump (Lab Alliance Series Π). A fixed volume of 10 mL of catalyst was used in all the studies. Prior to the activity test, the catalyst was reduced *in situ* under atmospheric pressure with hydrogen (120 mL/min) at 350 °C for 3 h. The reaction conditions was performed in the temperature range 100–300 °C, at a total pressure of 4.0 MPa, with a H_2/THN molar ratio of 12.16. After the reaction was maintained at the steady state for 1 h, the collection of products started in a trap at room temperature. After reduction to atmosphere pressure, the products were kept in sealed vials for off-line analysis.

2.4. Product analysis

Liquid products were analyzed on a gas chromatograph (GC) (Varian CP-3800) equipped with a capillary column (PONA) of 100 m in length and a flame ionization detector (FID). Identification of most of the reaction products was performed on a GC-MS (Agilent 6890-5973). Meanwhile, we compared those GC patterns with that in Sato's work [30].

In order to simplify the treatment of data, all the reaction products detected on our GC were grouped according their retaining time as follows:

(a) Lower molecules (LM): molecules with less than 10 carbons, including:

Light paraffins (LP): paraffins mainly containing 3–6 carbon atoms.

Light naphthenes (LN): naphthenes with less than 10 carbon atoms, such as methylcyclohexane, methylcyclopentane, ethylcyclohexane, propylcyclohexane, etc.

(b) C10 fractions:

Ring-opening products (ROP): alkyl-/alkenyl- cyclopentanes, cyclohexanes or benzenes such as butylcyclohexane and its isomers, pentylcyclopentane and its isomers, butylbenzene and its isomers, etc.

Ring contraction (RC): C10 compounds with two rings, and at least one of them was a C5 ring, which was contracted from C6 rings, such as methylindanes, methylindenes, 1,1′-bicyclopentyl decane, etc.

trans-decalin (*trans*-DHN): *trans*-decahydronaphthalene.
cis-decalin (*cis*-DHN): *cis*-decahydronaphthalene.
Naphthalene (NAP).

(c) Higher molecules (HM): molecules with more than 10 carbons, such as methyldecalins, methyltetralins, methylnaphthalenes, etc.

3. Results and discussion

3.1. Characterization of catalysts

XRD patterns (not shown here) of the K-USY samples with different K-loadings have been recorded. The loading of K did not produce new crystalline phase related with potassium even for K-loadings up to 2.0 wt.%. No distinct decrease in the relative crystallinity of the USY was observed. This means that K was highly dispersed on the USY. Table 1 presents the textural properties of the USY samples with different K-loadings. With an increase of the K-loading from 0 to 2.0 wt.%, no apparent changes of the specific surface areas were observed, and the micro- and meso-pore volumes showed only a slight decrease, from 0.21 to 0.20cm^3/g and from 0.15 to 0.12cm^3/g, respectively. By taking into account the results of the XRD patterns, it can be concluded that the introduction of K on USY up to 2.0 wt.% did not cause a blocking of the pores.

The effect of K addition on the acid sites was evaluated by NH_3-TPD and FT-IR spectroscopy of pyridine adsorption (results are shown in figure 1 and table 1, respectively). In figure 1, two distinct desorption peaks are shown in the profile of the USY, one of which centers at 240 °C and the other at 420 °C, corresponding to the weak and strong acid sites of the samples, respectively. By increasing the K loading, the amount of both the weak and the strong acid sites decreased obviously. However, the strong acid sites (the peak at 420 °C) changed more apparently than the weak acid sites. On the 2.0 K-USY sample, the remaining acid sites were found to be mainly weak acid sites. Thus, it is clear that K poisoned preferentially the strong acid sites.

The results of FT-IR spectroscopy of pyridine adsorption of the USY samples are given in table 1. It can be seen that all samples possessed both B (the band at 1545cm^{-1}) and L acid sites (the band at 1450cm^{-1}), with the former being the dominant. We can see that, on every sample with the degassing temperature increasing from 150 °C to 350 °C, the amounts of pyridine adsorbed on both the B and L acid sites decreased obviously. When the K loading was increased from 0 to 2.0 wt.%, the amounts of pyridine adsorbed on both the B and L acid sites decreased sequentially, especially the values at 350 °C decreased more markedly, indicating that weak acid sites was the dominant. On the 2.0 K-USY sample, the amounts of pyridine adsorbed on both the B and L acid sites were 639 and 91μmol/g at 150 °C, respectively, while those values decreased to 193 and 31μmol/g at 350 °C, indicating the remaining acid sites of this sample was almost weak B acid site after 2.0 wt.% K loading.

3.2. Catalytic performance

3.2.1. Influence of the reaction temperature

Severe hydrocracking reactions happened on 0.5 Pt/USY due its great amount of strong acid sites, and the reaction was very sensitive to temperature, so 0.5 Pt/0.4 K-USY was used to study the effect of temperature instead of K-free catalyst. Figure 2 shows the catalytic performance on the 0.5 Pt/0.4 K-USY catalyst as a function of temperature in the range of 100–300 °C. In figure 2a, it can be seen that in the range of 100–350 °C the conversion of THN was almost 100 wt.%, and the yield of HWM was negligible, which implied that this catalyst possessed a high activity, and was resistent to deactivation. Figure 2b shows the detailed distribution of C10 products for this catalyst in the same temperature range. It can be seen that at 100 °C, the THN converted completely to *trans*-DHN (28.4 wt.%) and

Table 1
Textural and acidic properties of USY samples with different K loadings

Sample	B.E.T. area (m^2/g)	Pore volume (cm^3/g)		Total acidity[a] (μmol NH_3/g)	Acidity[b] (μmol Py/g)			
		Micropore	Mesopore		Brönsted		Lewis	
					150 °C	350 °C	150 °C	350 °C
USY	498	0.21	0.15	1110	937	789	184	146
0.4 K-USY	477	0.20	0.14	987	753	510	159	99
1.2 K-USY	495	0.20	0.13	899	637	333	149	64
2.0 K-USY	487	0.20	0.12	707	639	193	91	31

[a] Amount of adsorbed NH_3 at 100 °C measured by NH_3-TPD.
[b] Acidity measured by adsorbed pyridine at different temperatures.

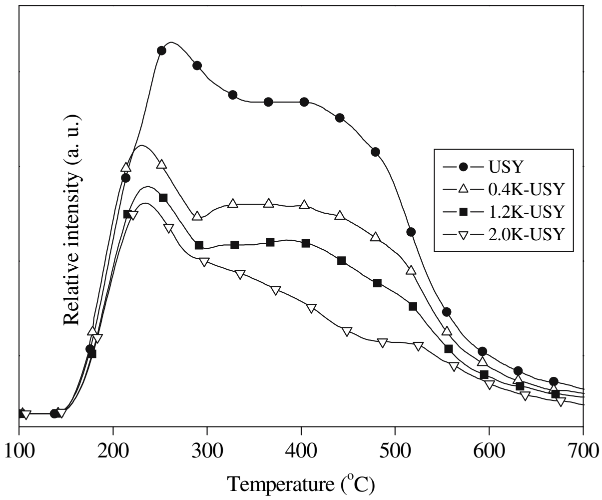

Figure 1. NH_3-TPD profiles of USY samples with different K loadings.

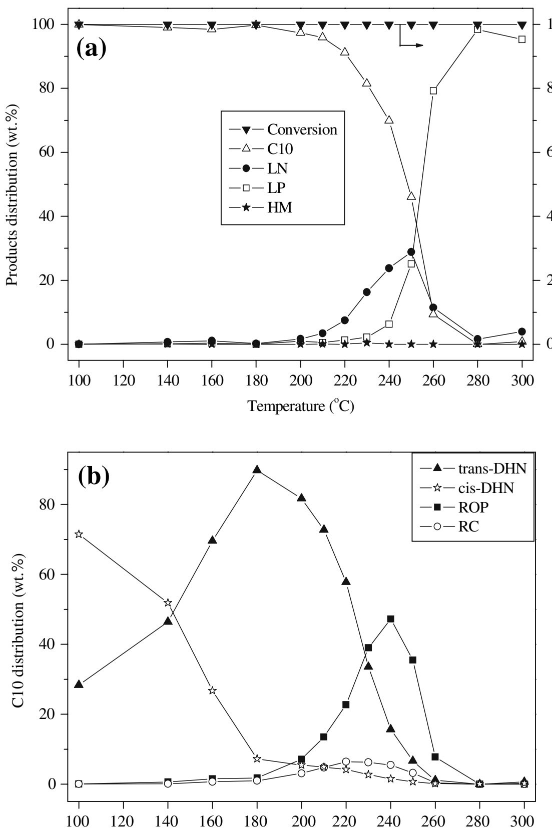

Figure 2. Catalytic performance of 0.5 Pt/0.4 K-USY as a function of temperature.

cis-DHN (71.5 wt.%). With the increasing of temperature from 100 °C to 140 °C, *cis*-DHN was the dominant product due to the geometrical factor for hydrogenation of double bond on metallic catalysts [31]. When the temperature was increased further to 180 °C, the yield of *trans*-DHN reached a maximum of 89.8 wt.% at 180 °C, due to the fact that *trans*-DHN isomers were thermodynamically more favored at this temperature. However, high selectivity of *cis*-DHN reported by Schmitz [26] was not obtained at this temperature, and the reason may be that their experiment was performed on a fixed reactor. Within this temperature range, only little amounts of ROP and RC were produced, and hydrogenation was the dominating reaction. With a further increase of the temperature up to 300 °C, the yield of C10 dropped sharply due to the occurrence of the cracking reactions, while that of LP increased remarkably. The yield of LN passed a maximum at 250 °C and then decreased, and finally converted to LP as a result of the hydrocracking reactions. These results indicated that the hydrocracking reaction was a sequential reaction of the ring-opening reaction. Within the above temperature range, the yield of ROP increased first, then passed through a maximum of 47.2 wt.% at 240 °C, while a low yield of C10 (69.9 wt.%) was obtained due to severe hydrocracking. At 300 °C, all of the C10 fractions reduced to zero, and hydrocracking became the wholly dominating reaction. All these results indicated that, in order to get high yields of both the ROP and the C10 fractions, deep hydrocracking reactions must be avoided. For this reason, it would be very important to investigate the functions of the metallic and acidic components of the catalysts in the present process of coupled hydrogenation and ring opening of THN.

3.2.2. Role of the metal sites

It is known that hydrogenation reactions can take place on noble metal sites [13], while the reaction of ring opening of THN is very complicated. To evaluate the role of the metal component in this reaction, catalysts with and without Pt loading were prepared and tested. The conversions of THN and the yields of C10 and ROP on the catalysts with different Pt loadings are shown in table 2. On the Pt-free sample, the conversion of THN was only 5.2 wt.%, and DHN was the dominating product. It implies that the hydrogenation of THN is able to occur on monofunctional acidic catalysts, but the rate was very low. Furthermore, no RC products were detected on this catalyst, indicating that with the existing of only acidic sites, ring contraction of the C6

Table 2

Catalytic activity (wt.%) of Pt/USY catalysts with different Pt loadings[a]

Pt loading (wt.%)	THN conversion	C10 yield	ROP yield
0	5.2	5.1	0
0.2	100	86.7	37.3
0.5	100	85.2	37.9
1.0	100	86.6	35.2

[a] Reaction conditions: T = 200 °C; P = 4.0 MPa; H_2/THN (mol/mol) = 12.16; LHSV = 1.98 h^{-1}.

ring to the C5 ring could not take place. On the other hand, severe hydrocracking of the hydrocarbons would happen on Pt-free catalysts at higher temperatures [32]. However, with the incorporation of the Pt, the conversion increased sharply to 100 wt.%, and RC products were detected, implying that the realization of ring contraction of the C6 ring to the C5 ring depended on the concurrent effects of both the metal and the acid sites, which was consistent with the results of Santikunaporn [7]. The yields of both C10 and ROP were enhanced simultaneously, since on bifunctional catalysts, hydrogenation can also occur on acid sites by means of the spilt-over hydrogen coming from the metal sites [13]. As the Pt loading was increased from 0.2 wt.% to 0.5 wt.%, the yields of C10 and ROP were maintained at ca. 86 and 37 wt.%, respectively. The results of Wang *et al.* [33] also confirmed that, once the Pt loading had reached a certain amount, the hydrogenation activities of the catalysts would not change significantly with the further improvement of Pt loading. When the Pt loading was 1.0 wt.%, a little decrease in the ROP yield was observed. It seemed that higher Pt loading would lead to the splitting of ROP due to the unbalance of the metallic and acidic centers. The conversion of THN on a Pd-Pt/Y catalyst in Sato's work [34] was only ca. 50 wt.%, this might be due to the presence of the 500 ppm dibenzothiophenes (DBT) in his feedstock, which could depressed the activity of the metal component. Thus, we can deduce that monofunctional acidic catalysts can catalyze partial hydrogenation of THN, but cannot catalyze ring contraction and ring opening under our experimental conditions. To achieve ring opening of THN, an optimal content of Pt should be incorporated. Accordingly, 0.5 wt.% of Pt was added to the catalysts in the following studies.

3.2.3. *Role of acid sites*

According to the mechanism of bifunctional catalysis [35], the acidic function plays an important role. However, the strong acid sites in USY would lead to severe hydrocracking of the reactants. For this reason, potassium is used as a basic component for tuning the acidic properties of the catalysts in this work. To study the influence of different acid sites on the catalytic activity, the product distributions of different catalysts at 250 °C were presented in table 3. On the 0.5 Pt/USY, the yield of ROP was only 1.7 wt.%, and 91.5 wt.% of the reactant had converted to LP, indicating the occurrence of severe hydrocracking. On the 0.5 Pt/0.4 K-USY, the introduction of 0.4 wt.% of K reduced the total number of the acid sites, especially the strong acid sites (as shown in figure 1). As a result, more ROP (35.5 wt.%) was obtained and less LM was produced, indicating that K had inhibited the hydrocracking reactions. When larger and larger amount of potassium was added, the yield of the hydrocracking products reduced continuously with the decreasing of the acid sites, with less LM and more C10 fractions being produced. On the 0.5 Pt/1.2 K-USY, a maximal ROP yield of 45.6 wt.% was obtained, indicating that the low strength of acid sites after potassium doping was favorable for the producing of the ROP even at higher temperatures. However, the yield of C10 was only 80.4 wt.%, and 19.5 wt.% of the reactant converted to LM, which were hydrocarbons outside the diesel range and should be restrained. On the other hand, though only a ROP yield of 21.4 wt.% was obtained on the 0.5 Pt/2.0 K-USY, a maximal C10 yield of 95 wt.% was achieved, indicating that the hydrocracking reactions were greatly eliminated on this catalyst, the acid sites of which were mostly weak acid sites (as shown in table 1). Under the present experimental conditions, with K loading increasing from 0 to 2.0 wt.%, the yield of RC, which was considered as an intermediate for ring opening, kept at a low level. From these results, we can conclude that, in order to get high yields of both ROP and C10, the acid properties of the bifunctional catalysts as well as the reaction conditions should be optimized carefully.

Table 3
Products distributions (wt.%) on catalysts with different K loadings at 250 °C[a]

	Catalysts[b]			
	0.5 Pt/ USY	0.5 Pt/ 0.4 K-USY	0.5 Pt/ 1.2 K-USY	0.5 Pt/ 2.0 K-USY
LP	91.5	25.1	3.4	1.0
LN	6.5	28.9	16.1	4.0
Products within C10				
ROP	1.7	35.5	45.6	21.4
RC	0.1	3.2	7.4	7.0
trans-DHN	0.2	6.7	25.2	61.5
cis-DHN	0	0.7	2.2	5.1

[a] Reaction conditions: $P = 4.0$MPa; H_2/THN (mol/mol) = 12.16; LHSV = 1.98 h^{-1}.
[b] The conversion of THN is 100 wt.% on every catalyst.

In the present process of coupled hydrogenation and ring opening of THN, as mentioned above, hydrocracking reactions such as dealkylation and β-fission of branch chains, etc., are sequential reactions of the ring-opening reaction and are responsible for the producing of low molecular weight hydrocarbons. From the viewpoint of achieving high selectivity for ring opening while maintaining the products in the diesel range, naphthenic rings in the feedstocks should be opened, but the hydrocracking reactions must be prevented. In the present study, we have found that on a series of 0.5 Pt/xK-USY catalysts ($x = 0$, 0.4, 1.2 and 2.0), the corresponding yields of ROP at a 90 wt.% C10 yield were 29.2, 31.2, 32.1 and 35.6 wt.%, respectively. It is clear that the ROP yield increased with the K loading, and the maximum (35.6 wt.%) yield was obtained on the 0.5 Pt/2.0 K-USY catalyst which possessed only weak acid sites (as shown in table 1). It was worth noting that the corresponding temperatures for achieving 90 wt.% C10 yield on the catalyst series of 0.5 Pt/xK-USY ($x = 0$, 0.4, 1.2 and 2.0) were ca. 210, 225, 240 and 260 °C, respectively. These results indicated that, in order to improve the cetane number and maintain the products within the diesel range, the strength of the acid sites should be tuned optimally, and bifunctional catalysts with only weak acid sites are favorable for selective ring opening and avoiding simultaneous hydrocracking even at rather high temperatures.

4. Conclusions

Pt/USY was an effective catalyst for the coupled hydrogenation and ring opening of THN. Hydrocracking was the sequential reaction of ring opening, leading to the diminishing of the ROP yield, and could be reduced by depressing the acid strength of the support. The acid properties of the USY support could be effectively tuned by potassium addition. As the K loading was increased from 0 to 2.0 wt.%, the number of acid sites decreased, especially for the strong acid sites, and the hydrocracking reactions were accordingly reduced. Thus, selective ring open of tetralin, with high yields of both C10 and ROP, can be realized on bifunctional catalysts with only weak acid sites. At a C10 yield of 90 wt.%, a maximum ROP yield of 35.6 wt.% was obtained on a 0.5 pt/2.0 K-USY catalyst at 260 °C.

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