

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.29>

Volume 3, Number 435 (2019), 49 – 55

UDC 541.128

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PROPANE-PROPYLENE OLIGOMERIZATION OVER MODIFIED PILLARED CLAY CATALYSTS

Abstract. Metal supported pillared clay catalysts were used in propane-propylene oligomerization. In the article was shown that the pillaring process has a significant impact on the carrier's nature. That is, specific surface area and porosity of the pillared clay were significantly increase compared with natural clay. The natural clay has lost its porosity at a temperature of 140 °C, reduce surface area from 62 to 20 m²/g. After pillaring this value increased to 110 m²/g. The catalysts exhibited good thermal stability at the calcination of 500 to 600 °C as indicated by its specific surface area. As well as, all synthesized catalysts showed selectivity to C₆ and C₉ olefins. The resulting mixtures of isoolefins provide a high-octane product that can be used as a mixture of environmentally friendly gasoline, jet and diesel fuel through hydrogenation.

Key words: pillared clay, propane-propylene fraction, fuel blending component, conversion, selectivity.

1. Introduction

According to the British Petroleum outlook report in 2016, the dependence of energy on crude oil will decrease to 30% by 2035 [1]. This means that in the future, alternative energy sources are more used. Oligomerization of light olefins is one direction of utilize residual gases from the oil refining processes (light FCC, Fisher-Tropsch synthesis of naphtha, etc.). In the oligomerization reaction it is more effective to use acid catalysts, like zeolites, ionic liquids and ion exchange resins. As well as, this reaction is also possible to perform in clay catalysts. Clay catalysts are natural, low cost and reusable, as well as does not cause any harm to the environment. Due to these advantages clay catalysts are widely used in oil refining [2-4].

Although, the most studied light olefin is ethylene, demand for propylene continues to grow. Propylene is a dissymmetric molecule, double bond on the carbon 1 (C1) or 2 (C2) allows it to obtain large amounts of dimer in the coordination of olefins to the catalytic metal center (see Fig. 1) [5]. Further, oligomerization is also developed with this mechanism. In propylene oligomerization products, linear oligomers are use for in diesel fuel additives, aromatics are use for solvents and detergents precursors. Recent years, demand for branched olefins is growing. The highly branched olefins (2,6-dimethylheptan-3, 2,6-dimethylheptan-2, 4,6-dimethylheptan-3, 2-methyloxan-2, 7-methyloctane-3) which obtained from the trimerization of propylene, are widely demanded for production of polymers. These products can be used in the production of plasticizers for plastics, especially the development of plastics with specific properties which will replacement of metal to plastic in aviation, automotive and military industries. And the tetramers of propylene are used in the production of lubricating oil additives. Research on this subject is more common in scientific literature of the last century [6-10]. Paul et al. the first reported that oligomerization of C₃ - C₄ olefins on nickel-substituted synthetic mica-montmorillonites (Ni-SMM). The Ni-SMM catalyst was extremely selective to high-octane products and showed corrosion and sulfur resistance [11]. Khamzin et al. reported pillared clay based super acidic catalysts use for oligomerization of propane –propylene fractions. The catalysts which were prepared by intercalation of montmorillonite

with zirconium, then modified with nickel. The 2.5% nickel modified pillared clay catalyst exhibited the best activity and selectivity in propylene trimerization [12]. Presently, Ni-exchanged pillared clays used as selective ethylene oligomerization. Hulea et al. elaborated the synthesis of acid washed (K10) and Al-pillared clays exchanged with nickel and tested them ethylene oligomerization reaction. They believed that the obtained results related to the textural and acid characteristics of the catalyst. The catalyst Ni-K10 exhibited superior catalytic behavior and higher selectivity to C₄ and C₆ linear olefins [13]. However, there are no publishing data on bimetal supported pillared clay catalysts use for propane-propylene oligomerization. In our previous publication, we reported investigation of the conversion of butane-butylene fractions on ruthenium and cobalt modified pillared clay catalysts [14]. Therefore, our present study was aimed to investigating catalytic properties of ruthenium and nickel supported pillared clay catalysts for propane-propylene oligomerization.

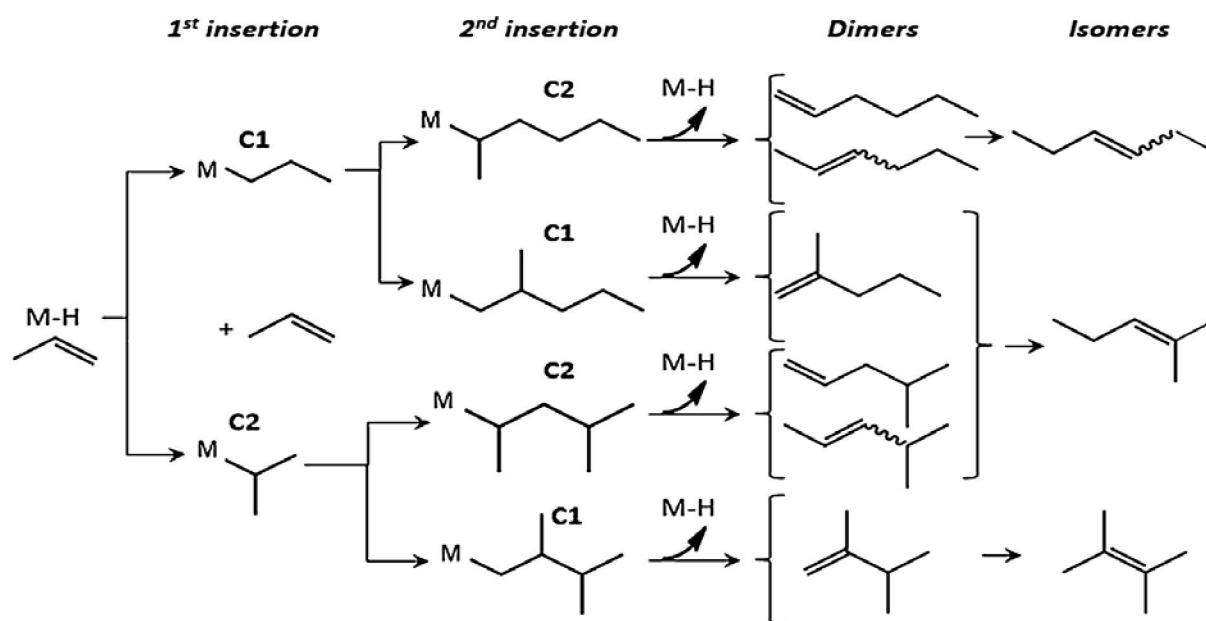


Figure 1 - Dimerization mechanism of propylene [5](M-H being a metal hydride)

Table 1 - Composition of Feedstock

Component	Quantity, %
Ethylene	2.1
Propane	19.2
Propylene	74.8
Total content of C ₄	3.8

2. Experimental

2.1. Materials

Bentonit (from South Kazakhstan, rich in montmorillonite > 90%). The cation exchange capacity is 66.4 mmol/100.0 g. clay. CrCl₃ (99%, Sigma-Aldrich), NaCl, Ruthenium (III) chloride (RuCl₃·3H₂O, 99.99%, Alfa-Aesar) and hexahydrate of nickel (II) nitrate (Ni(NO₃)₂·6H₂O). Materials in this experiment were used without further purification.

2.2. Catalyst preparation

For preparation of RuNi/MMC* catalyst system the aqueous solutions of ruthenium (III) chloride - RuCl₃·3H₂O and hexahydrate of nickel (II) nitrate - Ni(NO₃)₂·6H₂O were used. Pillared clay preparation carried out by method proposed in [15, 16]. Prior to pillaring process, the clay was saturate with sodium

ions through exchange with 1M NaCl for 8 h., and then washed with deionized water. The residue NaCl determined by the solution of AgNO₃. Then 0.1M NaOH solution was added to 0.1M CrCl₃ solution under vigorous stirring at room temperature. Concentration of chromium chloride change from 4.0 to 20.0 mmole Cr³⁺ per gram of clay. Then this mixture was added to aqueous clay suspension and stirred 4h. Obtained mass undergoes to drying in an air at ambient temperature and left for a few days, dried in air at 80 °C 8 hour, then calcined 450 °C with heating rate of 2 °C/min during 6h. Finally a certain mass of this sample is impregnated by nickel and ruthenium salts. The obtained mass was dried in the air (2 °C/min) at 80 °C for 8 hour and calcined at 450 °C during 6 h.

2.3. Characterization techniques

Chemical compositions of starting and modified clays were determined by XRF analysis. The textural properties of the samples were obtained from nitrogen adsorption-desorption isotherm, measured at 77K using an ASAP 200 Micrometric instrument. The specific surface area and porosity were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) - methods respectively.

2.4. Catalytic tests

The oligomerization of propane-propylene mixture was carried out in a stainless steel continuous flow fixed-bed reactor (inner diameter 5 mm). The temperature was monitored by using a K-type thermocouple that was inserted directly into the fixed bed and reaction pressure was controlled digitally using a Tescom back-pressure regulator. The reaction temperature and gas pressure are 110-170 °C and 4.0 MPa respectively. The crushed quartz was placed inside the reactor along with the catalyst. Prior to experiment the catalyst (1g) was pre-treated with stream of hydrogen (50 cm³/min) at 300 °C for 2 h. Then the reactor was cooled to reaction temperature with a flow of argon (Ar, 50 cm³/min) and the propane-propylene mixture were fed to the reactor and increasing the pressure to reaction conditions. Determination of feedstock (Table 1) and reaction products are analyzed by DANI Master GC Fast Gas Chromatograph equipped with a flame ionization detector (FID).

3. Results and discussion

The chemical compositions of starting and modified clays determined by XRF are listed in Table 2. The starting clay is composed of (by mass %): 59.15% SiO₂, 17.9% Al₂O₃, 6.41% Fe₂O₃, 1.03% MgO, 0.07% CaO and 2.56% Na₂O. After pillaring treatment, the exchangeable cations (Na⁺) were completely displaced by polyhydroxy complex of Cr³⁺, while Mg²⁺ content remained almost constant, not act as exchangeable cation.

The chemical, structural and textural characteristics of the modified clay and catalysts from its derived were widely examined in our previously report. They are belonging to type of pillared clay catalysts, with well ordered pillar and mesopore structure [17]. The main features of the catalysts prepared on this basis are shown in Table 3. In the table structural and adsorption characteristics of natural bentonite clay and the clay pillared with polyhydroxy complexes of chromium are summarized. The polyhydroxy complex of Cr, when modifying the natural clay led to the formation of columnar structures and give them a thermal stability at temperature of 500-600 °C.

Table 2 - Chemical composition (wt. %) of starting and pillared clays

Samples	Bentonite	Cr/Bentonite
SiO ₂	59.15	52.74
Al ₂ O ₃	17.9	15.98
Fe ₂ O ₃	6.41	6.30
MgO	1.03	1.0
CaO	0.07	-
Na ₂ O	2.56	0.02
Cr ₂ O ₃	-	10.63

Table 3 - Main properties of the starting and pillared clays

Amount of chromium, mmol/g clay	SSA, m ² /g	d ₀₀₁ , nm	Total pore volume, cm ³ /g	SSA at calcinations temperature	
				°C	m ² /g
-	62	0.9	0.10	140	20
4.0	160	1.82	0.36	300	130
8.0	220	1.96	0.42	450	190
12.0	250	2.38	0.46	500	220
16.0	270	2.6	0.47	600	240
20.0	250	2.15	0.43	600	230

*SSA-specific surface area

In our study, bentonite was modified with polyhydroxy complexes of chromium, which leads to a change in some physicochemical characteristics of this system. The non modified bentonite clay loses its porosity at temperature 140 °C with the surface area reduced from 62 to 20 m²/g. After pillaring, this value increased to 110 m²/g. The value of specific surface area of chromium pillared clay depends on amount of the polyhydroxy complex which give them a thermal stability at temperature of 500-600 °C. specific surface area of samples containing 12-20 mmol Cr³⁺ determined after heat treatment at 180 °C are 250-270 m²/g. The temperature increased 500 to 600°C was observed slightly reduces the value of their specific surface to 220-240 m²/g, respectively.

Pillared bentonite has a total pore volume of 0.36-0.47 cm³/g and interlayer distances of 1.82-2.6 nm. Compared with natural bentonite, where these values are - 0.10 cm³/g and 0.9 nm respectively. The highest values correspond to a chromium concentration about 12-16 mmol per gram of clay, where the polyhydroxy complexes of chromium are located between the layers. An increase in concentration of chromium above 20 mmol per gram of clay does not lead to further growth of the interlayer distance. This is probably due to the fact that in the solution non hydrolyzed forms of chromium salt do not affect the formation of layered-columnar structure.

The dependence of active metals in the catalyst on the product selectivity at different temperatures range shown in Figure 2. The reaction were conducted with different metal loading catalysts ranging from 0.5 to 2.0 wt.%. As you seen from the figure, almost all synthesized catalysts have shown good selectivity to C₆ and C₉ olefins. When the amount of active metal in the catalyst increases from 0.5 to 2.0% the selectivity of C₆ and C₉ decreases and selectivity of C₁₂ and C₁₅₊ increases. The highest selectivity catalyst for C₆ (170 °C, 59 %) and C₉ (150 °C, 35 %) was 1.0%RuNi/MMC and the highest selectivity catalyst for C₁₂ (110 °C, 16 %) and C₁₅₊ (170 °C, 3.1%) was 1.5%RuNi/MMC. Increase in the yield of C₁₂ and C₁₅₊ olefins is due to the increase of the hydrogen spillover by increasing the concentration of nickel and ruthenium onto the surface of the catalysts, which leads to cracking and other related reactions - disproportion of seal products. Additionally, taking into account the effect of the temperature to the product selectivity, in Fig. 2A and 2D can be seen, the increase in temperature was directly proportional to the formation of C₆ and C₁₅₊ olefins. In Fig. 2B and 2C, the temperature increase from 110 to 150 °C, the selectivity for C₉ increased, and the selectivity for C₁₂ decreased. Selectivity was opposite when the temperature continued rise to 170 °C.

The dependence of active metals on the conversion of C₃ fractions in various temperature ranges is shown in Figure 3. While the temperature rises from 110 to 170 °C, the conversion reaches a maximum value of at 150 °C (Fig. 3). Further increase in temperature had a negative effect on conversion. Also, it should be noted that the content of ruthenium and nickel is not directly proportional to the catalytic activity of the catalyst. When the content of ruthenium and nickel were 0.5-1.5 %, occurred an increase in conversion with increasing temperature, maximum attained with a 1.0 % content. Further increase to 2.0%, there was a decrease in conversion compared to others due to the transition of nanoscale particles to cluster structures.

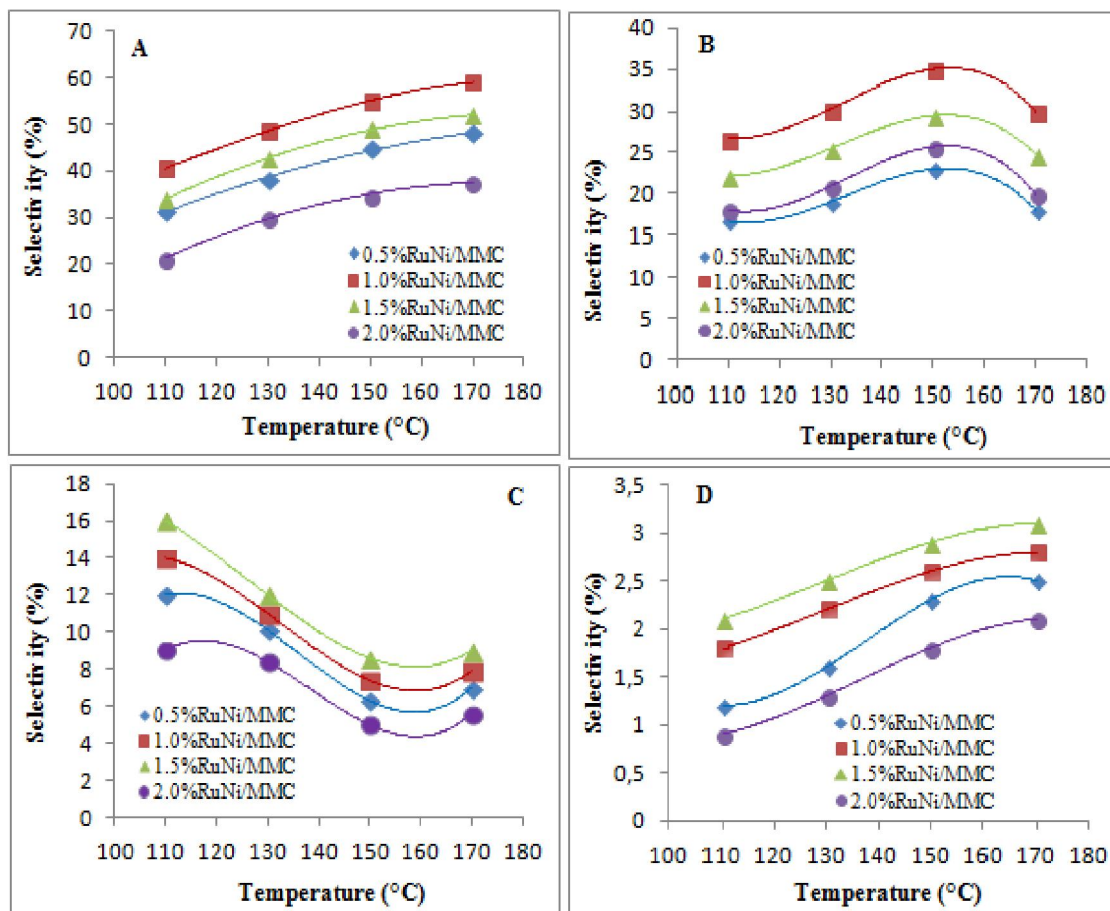


Figure 2. Dependence of isoolefin compositions (A – C₆; B – C₉; C – C₁₂; D – C₁₅₊) from the process temperature on the catalyst samples: (0.5 ~ 2.0 %) RuNi/MMC

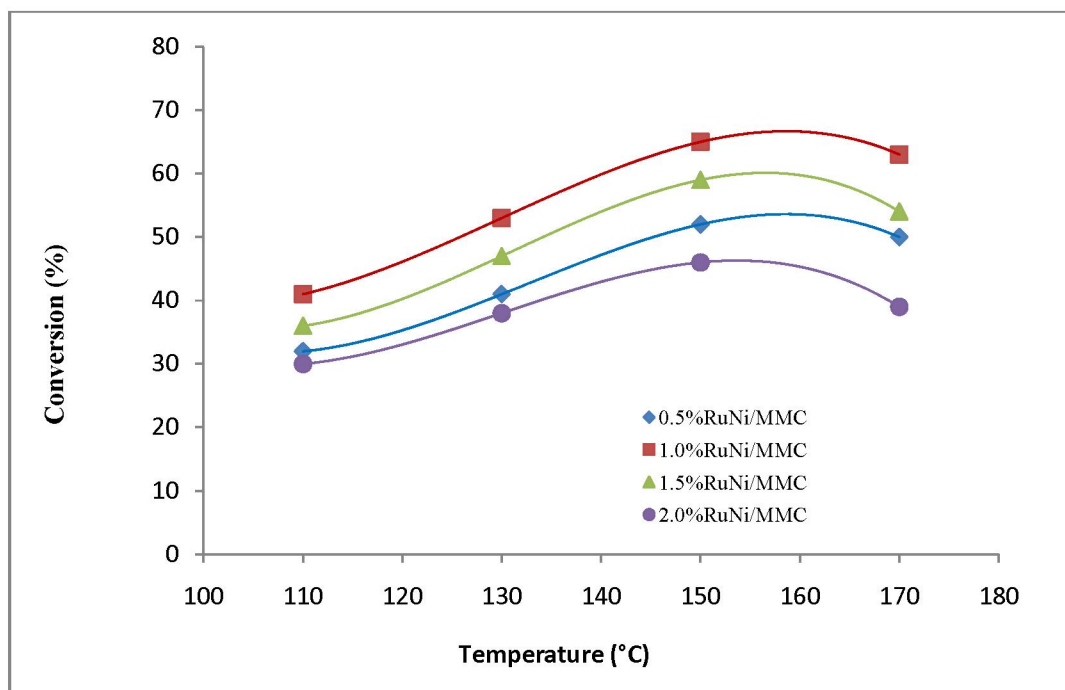


Figure 3 - Dependence of conversion of propane-propylene fractions to isoolefins from the process temperature on the catalyst samples: (0.5 ~ 2.0 %) RuNi/MMC

Conclusion

In propane-propylene oligomerization reaction were used metal supported pillared clay catalysts. It was found that the modified pillared clay catalyst samples had an optimal process temperature of 150 °C. The nature of the carrier was investigated by the role of pillaring agent and the active metal to be supported to the carrier. As a result of experiment, the pillaring of natural clay has significantly improved its textural properties and has shown good thermal stability at high temperatures (500-600 °C). The catalyst maintained its textural properties when further modified with active metals. As a result, synthesized all the catalysts were selective to C₆ and C₉ olefins. The resulting catalytic systems are of interest for simplicity of synthesis, the ability to widely vary the textural properties of the catalyst and the availability of raw materials - deposits of bentonite clay with a high content of montmorillonite exist in Kazakhstan.

УДК 541.128

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МОДИФИЦИРОВАННЫЙ КАБАТТЫЙ СТРУКТУРНЫЙ САЗ КАТАЛИЗАТОРАМИ ПРОПАН-ПРОПИЛЕНДИ ОЛИГОМЕРИЗАЦИИ

Аннотация. Пропан-пропилен олигомеризациясында металл отырғызылған тірек сазды катализаторлар қолданылды. Мақалада қабаттық құрылымдау процесінің тасымалдаушы сипатына айтарлықтай әсер ететіндігі көрсетілген. Яғни, табиғи саз балшыққа қарағанда қабаттық құрылымданған саз балшықтың арнайы беті мен кеуектілігі айтарлықтай артты. Табиғи саз балшық 140 °C температурада кеуектілігін жоғалтып, меншікті бетінің ауданы 62-ден 20 м²/г-ға төмендетеді. Бұл мән қабаттық құрылымдаудан кейін 110 м²/г дейін өсті. Меншікті бетінің ауданымен көрсетілгендей, катализаторлар 500-600 °C температурада кальцинация кезінде жақсы термиялық тұрақтылықты көрсетті. Сондай-ақ, барлық синтезделген катализаторлар C₆ және C₉ олефиндеріне біршама селективтілік көрсетті. Алынған изоолефин қоспасы гидрлеу арқылы экологиялық таза бензин, реактивті және дизель отыны қоспасы ретінде пайдаланылуы мүмкін жоғары октанды өніммен қамтамасыз етеді.

Түйін сөздер: қабаттық құрылымданған саз балшық, пропан-пропилен фракциясы, отынды араластыру компоненті, конверсия, селективтілік.

УДК 541.128

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ОЛИГОМЕРИЗАЦИЯ ПРОПАН-ПРОПИЛЕНОВАЯ ФРАКЦИЯ НА МОДИФИЦИРОВАННЫХ ГЛИНИСТЫХ КАТАЛИЗАТОРАХ

Аннотация. В пропан-пропиленовой олигомеризации применяли катализаторы на основе глины, нанесенный металлом. Было показано, что процесс пилларирования оказывает существенное влияние на природу носителя. То есть удельная площадь поверхности и пористость столбчатой глины значительно увеличились по сравнению с природной глиной. Природная глина потеряла свою пористость при температуре 140 °C, уменьшила площадь поверхности от 62 до 20 м²/г. После пилларирования это значение увеличилось до 110 м²/г. Катализаторы демонстрировали хорошую термическую стабильность при прокаливании от 500 до 600 °C, как указано ее удельной поверхностью. Все синтезированные катализаторы показали селективность по отношению к олефинам C₆ и C₉. Полученные смеси изоолефинов обеспечивают высокооктановый продукт, который можно использовать в качестве смеси экологически чистого бензина, реактивного и дизельного топлива посредством гидрирования.

Ключевые слова: столбчатая глина, пропан-пропиленовая фракция, компонент для смешивания топлива, конверсия, селективность.

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