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Development of $Pt/SO_4^{2-}/ZrO_2$ catalyst for isomerization of light naphtha

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Abstract

Platinum-loaded sulfated zirconium oxide catalyst ($Pt/SO_4^{2-}/ZrO_2$) for isomerization of light naphtha had been developed through the joint research between Cosmo Oil Co., Ltd., and Mitsubishi Heavy Industries, Ltd., in 1983. The role of small amount of noble metal in this novel catalyst is presented. Platinum improved catalyst stability by preventing formation of coke precursors on strong acid site of sulfated zirconium.

After the collaboration for commercialization of this catalyst with UOP LLC for many years, we had reached to a success of the first commercial operation for naphtha isomerization catalysts in 1996. The expected performance and stability during the commercial operation of Par-Isom have been obtained.

Keywords: Isomerization; Light naphtha; $Pt/SO_4^{2-}/ZrO_2$

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1. Introduction

The next coming gasoline regulations for sulfur content and Reid vapor pressure (RVP) related to volatile organic compounds (VOCs) have been determined because global environmental concern leads to increasing requirement for severe quality of gasoline. Additionally, the new regulation for aromatic compounds and olefins in gasoline has been discussed. The other high-octane gasoline blend stocks will be surely required under these regulations, which will put too great a burden on refinery. Therefore, the production of paraffin based high-octane gasoline blend stock such as isomerate from isomerization of light naphtha might be a key technology for gasoline supply to cope with future gasoline regulations. Table 1 shows the schedule for gasoline regulations in Japan. Sulfur content, benzene content and RVP have been restricted under 100 ppm, 1 vol.% and 72 kPa, respectively. Although aromatics and olefins in gasoline have not been regulated yet, we must consider them in the future. Regarding MTBE, all Japanese petroleum industries have refrained from blending it due to environmental affairs. Further regulation for sulfur (<50 ppm) and RVP (<65 kPa) will start in 2005. These regulations will bring certain change in gasoline blend stocks. An example of countermeasures for each regulation is shown in Fig. 1. For the future regulation of sulfur, the hydrodesulfurization of FCC gasoline (FCCG) will be needed. It is important to keep high-octane number of FCCG through the hydrotreating. An enforcement of RVP regulation will diminish using butane as a high-octane component. Regulations of aromatics and olefins in gasoline will result in a restriction of use of FCCG and reformate. All of these cases will bring a shortage of gasoline and a lack of its octane number. Isomerization of naphtha is composed mainly of a conversion of *n*-pentane and *n*-hexane into *iso*-pentane, mono-methyl and

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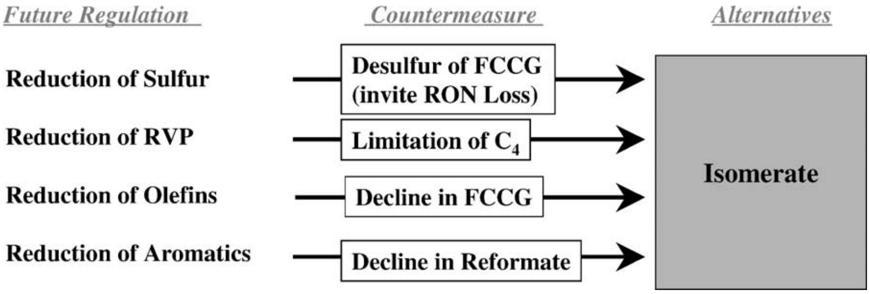

Fig. 1. Isomerate for the candidate of countermeasures for each gasoline regulation.

Table 1
Schedule for gasoline regulation in Japan

Gasoline	Year			
	1991	1999	2001	2005[a]
Sulfur	100 ppm	→	→	50 ppm
RVP[b]	78 kPa	→	75 kPa	65 kPa
Benzene	5 vol.%	1 vol.%	→	→
Aromatics	←	No regulation		→
Olefins	←	No regulation		→
MTBE	7 vol.%	→	None[b]	→

[a] Next regulations from 2005 are not decided yet.

[b] RVP and MTBE are voluntary controls of Japanese petroleum industries.

di-methyl pentane. Di-methyl hexane has higher RON than that of mono-methyl hexane, and is preferentially produced at low temperature subject to chemical equilibrium. So, in isomerization reaction, lower reaction temperature is more preferable.

Cosmo Oil Co., Ltd. and Mitsubishi Heavy Industries, Ltd. have developed a new solid acid catalyst, which reveals higher activity for light naphtha isomerization at lower temperature and is less sensitive to the amount of water in feed oil than conventional catalysts. This technology has been licensed to UOP LLC, and they have finally succeeded in development of a new isomerization process of light naphtha with the licensed $Pt/SO_4^{2-}/ZrO_2$ catalyst and have released this process as Par-Isom [1].

2. Development of $Pt/SO_4^{2-}/ZrO_2$ catalyst

2.1. *Target for catalyst development*

Commercial isomerization process of light naphtha has been already installed more than 1,400,000 BPD capacity in the world by 2000. Two types of catalyst had been used for naphtha isomerization in commercial process before we developed $Pt/SO_4^{2-}/ZrO_2$ catalyst, chlorided alumina catalysts, and zeolite catalysts. The Penex process using platinum-loaded chlorided alumina catalyst provides about 83 RON isomerate at low operating temperature around 140 °C. However, it is necessary to feed some organic chloride chemicals for keeping catalyst activities during the operation. In addition to this problem, expensive dryers for both feed oil and make-up hydrogen are required since the catalyst is very sensitive to the amount of water in feed oil. On the other hand, the Hysomer process using platinum-loaded zeolite catalysts required higher operating temperature more than 250 °C. Therefore, octane number of isomerate produced by this process will be up to about 78 RON due to equilibrium limitation.

Our target for the catalyst development was to achieve both high activity and less sensitivity to the water at low temperature without any chemicals. History of our catalyst development is summarized in Table 2. Cosmo Oil Co., Ltd. and Mitsubishi Heavy Industries, Ltd. started joint research in RAULO

Table 2
Development of the $Pt/SO_4^{2-}/ZrO_2$ catalyst

1983	Participated in ex-RAULO (sponsored by METI in Japan) and found the $Pt/SO_4^{2-}/ZrO_2$ catalyst
1986	Establishment of prototype of the $Pt/SO_4^{2-}/ZrO_2$ catalyst
1990	Start of joint development with UOP for commercial process
1996	UOP released the LPI-100 catalyst and the Par-Isom process and the first commercial operation at Flying J Ref. in USA

sponsored by METI in Japan, and we developed Pt-loaded sulfated zirconium oxides catalyst in 1983. After the establishment of prototype of the catalyst [2], collaboration to commercialize this new catalyst started with UOP LLC in 1990.

After we established an industrial catalyst and a commercial process, UOP LLC released the LPI-100 catalyst composed of Pt/SO_4^{2-}/ZrO_2 and the Par-Isom process into the market, respectively since 1996. The first commercial operation of the Par-Isom process using the LPI-100 catalyst started in the refinery of Flying J Company at North Salt Lake City of USA in December 1996.

2.2. Impact of Pt loading on SO_4^{2-}/ZrO_2 catalyst

At first we investigated the sulfated zirconium oxide catalyst that had reported as the solid acid suitable for isomerization [3]. The activity of SO_4^{2-}/ZrO_2 catalyst for *n*-pentane isomerization is shown in Fig. 2. This test was carried out using a fixed-bed reactor under the following conditions: at 140 °C, 2 MPa of hydrogen pressure, and a hydrogen to *n*-pentane mole ratio of 1.5. The result indicated that the SO_4^{2-}/ZrO_2 catalyst had high activity at initial period but the activity declined rapidly. We assumed that this deactivation was due to the formation of coke precursors over the strong acid sites. Subsequently we started to research the effect of the applying of noble metals because they had the hydrogenation activity for stabilization of the SO_4^{2-}/ZrO_2 catalyst. As a result, we have succeeded to improve the stability of the SO_4^{2-}/ZrO_2 catalyst by loading of a small amount of the noble metal. As shown in Figs. 2 and 3, loading of Pt improved the stability of the SO_4^{2-}/ZrO_2 catalyst and reduced coke formation. Increasing the amount of Pt enhanced these effects, the maximum isomerization activity was obtained at 0.5 mass% of Pt loading. Therefore, we supposed that Pt on the SO_4^{2-}/ZrO_2 catalyst promoted to remove the coke precursors from the catalyst surface and kept the isomerization activity. Although similar effects were observed for other novel metals such as Pd, Ru, Ni or Rh, Pt indicated the highest effects among them. The effects of Pt loading on the SO_4^{2-}/ZrO_2 catalyst for isomerization have been reported also by another researchers after our work [4–21].

2.3. Comparison between Pt/SO_4^{2-}/ZrO_2 catalyst and conventional catalysts

Fig. 4 shows the activity of *n*-pentane isomerization of our developed Pt/SO_4^{2-}/ZrO_2 catalyst comparing with the conventional catalysts. The activity of our developed catalyst was higher than that of the zeolitic catalyst but lower than that of the chlorided alumina catalyst. This result could be caused by the difference

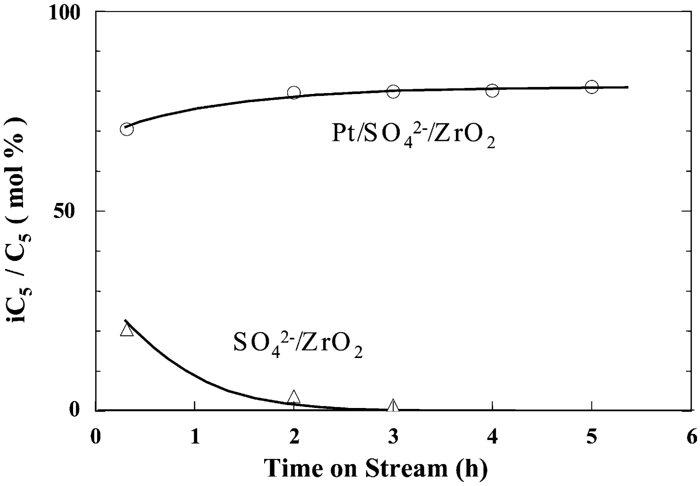

Fig. 2. Stabilization of SO_4^{2-}/ZrO_2 catalyst by loading of Pt in *n*-pentane isomerization (140 °C, 2 MPa, LHSV 1.5 h^{-1}, H_2/nC_5 = 1.5).

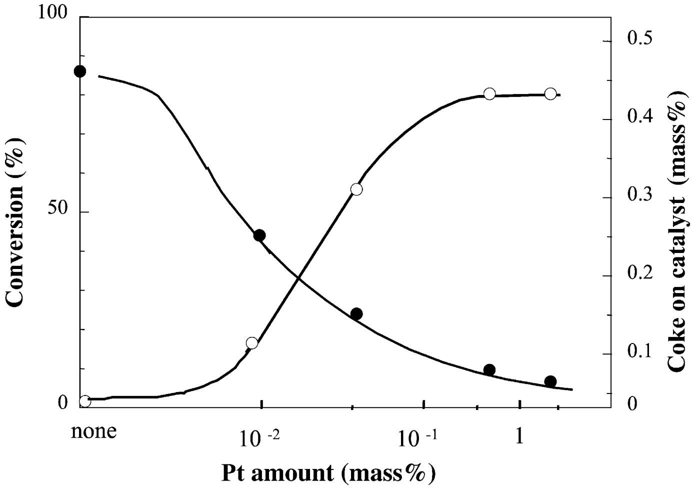

Fig. 3. Correlation between (○) conversion or (●) coke and Pt amount on SO_4^{2-}/ZrO_2 catalyst in *n*-pentane isomerization (140 °C, 2 MPa, LHSV 1.5 h^{-1}, $H_2/nC_5 = 1.5$).

of the acid type of these catalysts. For instance, the solid acid sites of the chlorided alumina catalyst would be same as those of the catalyst for Friedel–Crafts reaction that work at lower temperature, on the other hand, the active sites of the zeolite catalyst would perform at higher temperature instinctively.

Fig. 5 shows the comparison of the light naphtha isomerization activity between the $Pt/SO_4^{2-}/ZrO_2$ catalyst and the Pt-loaded zeolite catalyst (Pt/zeolite) at the same amount of Pt loading (0.5 mass%). Evaluation of the relationship between RON and liquid yield is important for the commercial units, because

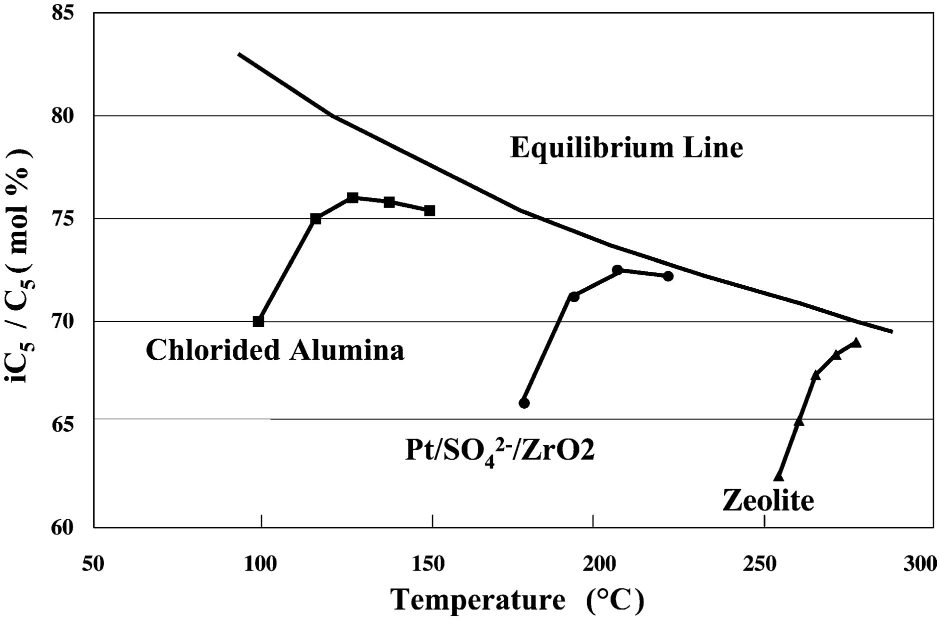

Fig. 4. Temperature dependency between conventional catalysts and the $Pt/SO_4^{2-}/ZrO_2$ catalyst in *n*-pentane isomerization.

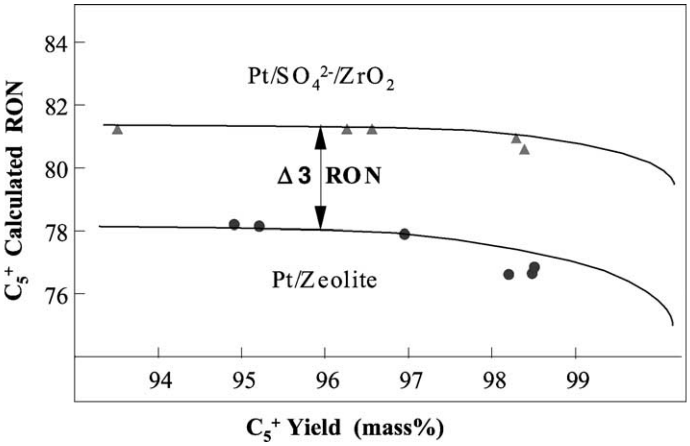

Fig. 5. Catalyst comparison of calculated RON vs. liquid yield in *n*-pentane isomerization.

both the reaction temperature and the selectivity of the catalyst affect them. Higher reaction temperature would cause the cracking that result in lower selectivity of the liquid product and higher by-product yield such as propane and butane. RON of isomerate obtained by Pt/SO_4^{2-}/ZrO_2 was three-point higher than in the case of Pt/zeolite at the same liquid yield. We supposed that higher RON of Pt/SO_4^{2-}/ZrO_2 could be due to the lower reaction temperature than Pt/zeolite.

2.4. Tolerance to water

Influence of water content in feed naphtha is shown in Fig. 6. The experiment was continuously conducted with the same catalyst by changing feed oil by turns. For this evaluation, we varied the water content in feed oil with 0, 10 and 35 ppm. As shown in Fig. 6, Pt/SO_4^{2-}/ZrO_2 had a good tolerance to water up to 35 ppm that was same as the saturated water content in light naphtha. In more detail, the activity in the case of

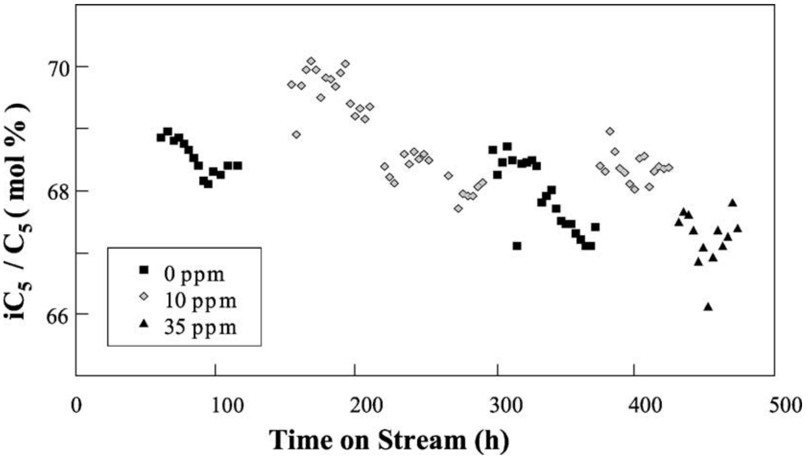

Fig. 6. Influences of water in the feed oil for the Pt/SO_4^{2-}/ZrO_2 catalyst in *n*-pentane isomerization (204 °C, 1.7 MPa, LHSV 3 h^{-1}, H_2/nC_5 = 2).

10 ppm water was slightly higher than that in the case of water-free. As the result, it was confirmed that the water tolerance of Pt/SO_4^{2-}/ZrO_2 was same as that of Pt/zeolite and stronger than that of the chlorided alumina catalyst.

3. Development of new process for light naphtha isomerization

3.1. Features of the Par-Isom process

Fig. 7 shows the flow diagram of the Par-Isom process, which is same as the general reaction system of hydrodesulfurization of light naphtha. Hydrogen is introduced to the reactor after the heater for that we can utilize not only the furnace but also the heat exchanger. The LPI-100 catalyst composed of Pt/SO_4^{2-}/ZrO_2 is loaded in the fixed-bed reactor. Separated hydrogen-rich gas can be recycled to the reactor and isomerate is introduced to the stabilizer in order to adjust the vapor pressure. Performances of current commercial processes and catalysts are summarized in Table 3. The LPI-100 catalyst can be used at lower reaction temperature and higher space velocity than the zeolitic catalyst for the Hysomer process. On the other hand, the Par-Isom process with the LPI-100 catalyst can allow using the water-saturated naphtha as the feedstock without the dryer, while feed naphtha and make-up hydrogen have to be dried completely for the Penex process. This characteristic would reduce the capital investment and the operation cost lower than those for the Penex process. Regarding sulfur content in feed, all these isomerization processes need hydrodesulfurization of feed oil because sulfur compounds are harmful for all the catalysts, however, sulfur tolerance of the LPI-100 catalyst is same as that of zeolitic catalyst while the chlorided aluminum catalyst is very weak to sulfur. Each process increases RON of light naphtha to 84 in the Penex process, to 81 in the Par-Isom process, or to 77 in the Hysomer process, respectively. The LPI-100 catalyst and the zeolitic catalyst are fully regenerable using the simple oxidation procedure.

Table 3
Comparison between conventional and the Par-Isom process for light naphtha isomerization

Process catalyst	Penex Pt/Al_2O_3	Par-Isom Pt/SO_4^{2-}/ZrO_2	Hysomer Pt/zeolite
Feed limitations			
Sulfur (mass ppm)	<0.1	<20	<20
Water (mass ppm)	<0.1	<30	<30
Aromatics (mass%)	<2	<2	<3
C_7^+ (mass%)	<2	<2	<2
Reaction conditions			
Temperature (°C)	120–160	180–240	220–300
Pressure (MPa)	3	3	3
LHSV (h^{-1})	1–2	3	2–3
Performances (isomerate)			
Yield (mass%)	99	98.5	98
RON	83	81	77

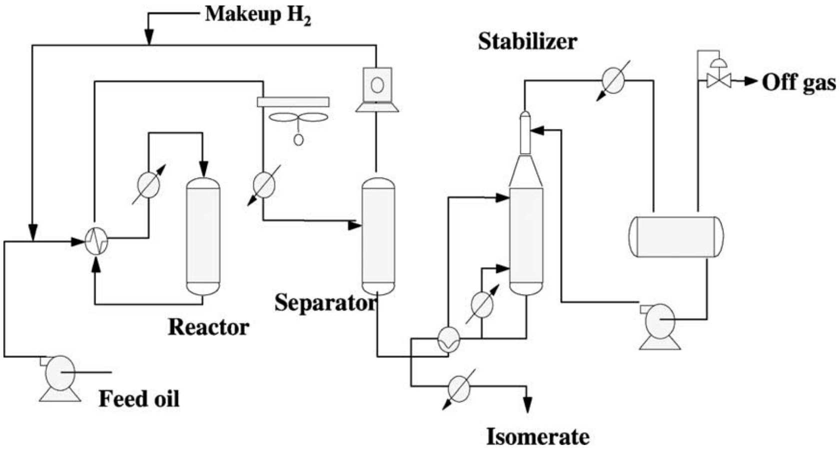

Fig. 7. Flow scheme of the Par-Isom process.

Table 4
Commercial performance of the LPI-100 catalyst [22]

Catalyst	Zeolite	LPI-100	Benefit
Capacity (BPD)	825	900	+9%
Product C_5^+ RON	76.9	79.3	+2.4
Yield (mass%)	91.7	96.5	+4.8

3.2. Commercial experience

In 1996, the first commercial application of the LPI-100 catalyst was accomplished at the existing zeolitic isomerization process unit in the refinery of Flying J Company at North Salt Lake City of USA. Any other portion of the plant except the catalyst were not changed or modified. Actual operation results are summarized in Table 4 [22]. Reaction conditions except for the temperature are almost same as those of the previous zeolitic catalyst process. The LPI-100 catalyst improved liquid yield and RON at lower temperature than the previous zeolitic catalyst.

4. Summary

In the future, an environmental problem will become more critical all over the world. Regarding motor gasoline, isomerization of light naphtha would be an important solution for clean gasoline production. Our developed isomerization catalyst “LPI-100” and process “Par-Isom” could help all refiners to produce the environmental friendly gasoline blend stock economically.

In actual, the Par-Isom process with the LPI-100 catalyst has been installed continuously in the world since the first commercial experience.

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