Highly Selective Synthesis of High Octane-Number Gasoline from Light Olefins on Fe-Silicates

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(Received October 23, 1986)

The conversion of light olefins such as ethylene, propylene, and butenes to gasoline was investigated with various metallosilicates having a pentasil pore-opening structure. The metallosilicates were prepared using a novel rapid crystallization method by replacing the Al ingredient in the H-ZSM-5 with various metal salts at the gel formation stage. The silicates of Al (i.e., H-ZSM-5), Ga, V, Cr, and Zr were not highly effective for selective conversion to liquid products because of a significant formation of gaseous C_1 - C_4 paraffins accompanied with the formation of aromatics. On the other hand, Fe-silicates were highly effective for selective formation of liquid products in the gasoline fraction. For example, 95.6% propylene fed was converted under the space velocity of $4,500\text{ h}^{-1}$ and at 300°C to the liquid products with a space-time yield as high as $8.09\text{ kg/l}\cdot\text{h}$. The octane-number of the gasoline produced was as high as 95 because of the high percentage of branched internal-olefins found in the liquid products. The Fe-silicate exhibited high activity and selectivity under various conditions, and maintained its steady performance at least 100 h on stream. The reason for this high gasoline selectivity of Fe-silicate was discussed in relation to its properties and performance in methanol conversion to hydrocarbons.

1. Introduction

Since the oil crisis, heavy oil has been replaced by coal in the steel industries, and in the electric power and other large scale energy generation systems. Accordingly, the excessive supply of heavy oil has become a serious problem, and to develop new routes for effective utilization of heavy oil has become of great significance. This paper concerns with the subject and aims at developing a new synthesis route for high octane-number gasoline from light olefins which are produced by thermal cracking of heavy oil.

Conventional processes for thermal cracking of residual oil produce considerable amounts of light olefins besides gasoline, kerosene, light oil, and coke.¹⁾ Since the yield of gasoline (C_5 - C_{11} hydrocarbons) is not high enough in the conventional processes, successive conversion to gasoline of the light olefins is expected. As conventional catalysts for polymer gasoline synthesis from light olefins, solid phosphoric acid, supported nickel oxide, and sulfuric acid are known.^{2),3)} From the industrial

point of view, however, the performance of these catalysts is insufficient because of such negative factors as low activity for and selectivity to gasoline formation, short catalyst life, corrosive action on the reactor, and low octane-number of the gasoline produced.⁴⁾

Recently, it has been reported that H-ZSM-5 is effective for conversion of light olefins to gasoline fraction⁴⁾⁻⁹⁾; however, its selectivity to gasoline fraction is inadequate because it forms considerable amounts of gaseous light paraffins (C_1 - C_4) accompanied with the formation of aromatics.^{4),5),8),9)} The aromatization activity of H-ZSM-5 is due to its strong acid sites brought about by the Al cations in ZSM-5.¹⁰⁾⁻¹²⁾

In order to modify the acidic properties and pore diameters, we replaced Al with other elements with maintaining a pentasil pore-opening structure and three dimensional pore connection of ZSM-5.^{4),8),9),13),14)} This was done because such pore structure of ZSM-5 is considered to be the reason for shape selectivity and long catalyst life.^{15),16)} Though metallosilicate synthesis has also been studied by other authors¹⁷⁾⁻¹⁹⁾, its application to cat-

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Fig. 1 Schematic Diagram for the Continuous Flow Reaction Apparatus (a) and Details of the Liquid Trap (b)

alytic reactions has not yet been investigated extensively. The effect of such metal replacement on the selectivity to hydrocarbons from methanol has been reported in our previous papers.^{8),13),14)}

In this paper, we described the effect of metal replacement on light olefin conversion; also we focused our interest on the performance of Fe-silicate which exhibited the most best result for gasoline synthesis among the various metallosilicates tested.

2. Experimental

Catalysts: H-ZSM-5 was prepared by the rapid crystallization method⁸⁾, and various kinds of metallosilicates were prepared by replacing the Al ingredient with other metal salts at the gel-formation stage of the ZSM-5 preparations. Principles and concrete procedures have been described in detail in our previous papers.^{4),8),13),14)} All the catalysts in a grain-size of 7–15 mesh were used as the protonated form.

Fe-silicates with various Fe contents were prepared by adopting also the rapid crystallization method.¹⁴⁾ The observed Fe concentrations in the products were almost equal to those of the charged materials, and increased with increasing charged concentration of Fe in the starting materials up to the Si/Fe ratio 12 (10 wt% as Fe_2O_3). Since the X-ray diffraction patterns of Fe-silicates were almost the same as the pattern of ZSM-5, various amounts of Fe are incorporated in the silicate

crystal having the pentasil structure. In consistent with recent investigations of Fe-silicate with solid state MAS NMR²⁰⁾, ESR spectra of the Fe-silicate suggests that Fe ion be highly dispersed in the crystal, and a considerable part of Fe^{3+} ions occupies the framework of silicate crystal. The color of Fe-silicate (milk-white even for the catalyst with the highest Fe content) and the negligible activity for CO hydrogenation are in accordance with the idea. TPD spectra of NH_3 from the Fe-silicates indicated that the Fe ion incorporated in the crystal was responsible for the formation of acid sites, and the acid strength of Fe-silicate was weaker than that of H-ZSM-5. Furthermore, SEM (scanning electron microscope) and EPMA (electron probe micro-analysis) measurements indicated that a small amount of Fe acted as the nucleus in the growth of high-silica crystal to change the morphology and that the Fe concentration inside the crystal was higher than the concentration at outer surface layers of the crystal particulate. Detailed data of these observations have been described in our previous paper.¹⁴⁾

Apparatus and reaction method: An ordinary continuous flow reaction apparatus was used under atmospheric pressure. A schematic diagram of the apparatus and the liquid-products trap immersed in an ice-water bath are shown in **Fig. 1(a)** and **Fig. 1(b)**, respectively. A 1.0 g (or ca. 1.5 ml) portion of the catalyst was packed in a transparent quartz tubular reactor of 8 mm inner diameter and pre-

treated with an N_2 flow at 500°C for 30 min to normalize the catalyst surface conditions by removal of the adsorbed H_2O . A reactant gas was fed to the reactor, and the gas produced was led to the cooled trap. The integrated formation rate of liquid products was determined by measuring the amount of the liquids during a definite time on stream, while the formation rate of gaseous products was determined by measuring the flow rate using a soap film flow meter. The liquid and gaseous products were analyzed by using three gas chromatographs simultaneously. Columns of MS-5A, VZ-10, and Silicone-OV-101 were used to analyze the whole range of hydrocarbons produced and hydrogen. Each gas chromatograph was equipped with an integrator. Research octane number of the liquid products was measured conventionally according to the formula of JIS K-2280.

The reaction was carried out under the following conditions: reactants: ethylene, propylene, or butenes; reaction temperature: 260–360°C; space velocity 900–4,500 h^{-1} ; and N_2 was used as the diluent when needed.

3. Results and Discussion

3.1 Comparison of Performance of Various Metallosilicates for Propylene Conversion

The results of propylene conversion performance on various metallosilicates were compared by using a feed gas mixture of 17% C_3H_6 – 83% N_2 . All the metallosilicates used exhibited activities adequate for propylene oligomerization, and attained conversion level above 96% at temperatures as low as 295°C. The product distribution for each catalyst is shown in **Fig. 2**. Among the hydrocarbons produced, butenes, C_5 – C_{11} aliphatics, and aromatics

were trapped mainly in the ice-cooled trap, while light paraffins (C_1 – C_4) and ethylene were found mainly in the gas phase. Thus, we define, hereafter, the hydrocarbons trapped in the ice-cooled trap as liquid products in discussing changes in product distribution with the catalyst. A typical H-ZSM-5, Al-silicate having Si/Al ratio 40, yielded considerable amounts of aromatics and C_1 – C_4 paraffins in addition to butenes and C_5 – C_{11} aliphatics. The Ga-silicate of a high Ga content (Si/Ga=40) gave substantially similar results, although the amounts of aromatics and light paraffins decreased somewhat. Low metal-content metallosilicates (Si/Metal=3,200), except Fe-silicate, gave similar results to those of H-ZSM-5 of low Al content. On the other hand, the Fe-silicate gave a significantly different product distribution, i.e., traces of light paraffins were formed, and the selectivity to liquid products was very high. All light paraffins and butenes dissolved in the gasoline fraction. From the comparison of the results of low- and high-metal-content catalysts, any remarkable change in product selectivity would not be expected by merely changing the metal content; only the kind of metal, especially Fe, incorporated in the silicate crystal could bring about any significant improvement in the product selectivity for gasoline synthesis.

3.2 Effect of Si/Fe Ratio in Fe-Silicate on Performance

To confirm the excellent performance of the Fe-silicate more precisely, propylene conversion on Fe-silicates with different Si/Fe ratios was performed using nondiluted propylene as the reactant. Other reaction conditions were similar to those of experiments described above.

The product distributions are shown in **Fig. 3**. Notwithstanding the use of nondiluted propylene, the conversion was almost complete for all catalysts compared. As for H-ZSM-5's, although the selectivity to aromatics increased and that to C_1 – C_4 paraffins decreased compared with the results of the experiments using diluted propylene, there was no significant change in the product distribution between the two H-ZSM-5's, Si/Al=3,200 and 40. On the other hand, in the case of Fe-silicates, when the Si/Fe ratio was 3,200 or 12, the selectivity to C_1 – C_4 paraffins was very low, but the Fe-silicates having Si/Fe ratios 400 and 40 gave similar results as did the H-ZSM-5's.

In our previous paper¹⁴), we described the dependence of the number of strong acid sites on the Fe content of Fe-silicate based on the results of TPD

Feed gas, 17% propylene and 83% N_2 ; temperature, 295°C; SV, 900 h^{-1}

Fig. 2 Product Distribution in the Propylene Conversion on Various Metallosilicates and H-ZSM-5's

Fig. 3 Product Distribution in the Propylene Conversion on Fe-Silicates and H-ZSM-5's with Different Si/Metal Ratios

measurements for adsorbed NH_3 . According to this dependence, the number of strong acid sites increases with increase in the Fe content as Fe_2O_3 up to about 5 wt%, the number of strong acid sites decreases with further increase in the Fe content. Fe-silicates of higher Fe contents lacked sufficient crystallinity compared with the others. This feature related to the number of strong acid sites is reflected on the selectivity of aromatics and light olefins from methanol; namely, aromatics and light paraffins increase with increasing number of strong acid sites and *vice versa* for light olefins. The results of propylene conversion observed in this study are in good accord with those of methanol conversion considered from the viewpoint of the relation between the number of acid sites and the yields of aromatics or of $\text{C}_1\text{-C}_4$ light paraffins.

The principal reaction scheme for methanol conversion to hydrocarbon on H-ZSM-5 has been proposed based on the results in accord with a number of researchers^{(10),(11),(21),(22)} as follows:

and it is obvious that strong acid sites on H-ZSM-5 are responsible for the aromatization from light olefins and also for the hydrogenation of light olefins with the hydrogen formed accompanying aromatization.^{(12),(23)}

The latter half of the above reaction scheme would be considered as olefin conversion on H-ZSM-5 although there are no methanol and/or dimethyl ether and water in the reactant. Actually, the result of olefin conversion on H-ZSM-5 can well be implied by this reaction scheme. However, the

main reaction path on the Fe-silicates having Si/Fe ratios 3,200 and 12 lacks aromatization and hydrogenation, indicating that the nature of acid sites is different from that of H-ZSM-5, i.e., somewhat weaker than H-ZSM-5 as we have observed in the NH_3 -TPD profiles.^{(14),(24)}

3.3 Extension to Butenes and Ethylene Conversions

Butenes were converted on the catalysts used in the propylene conversion under the same temperature and space velocity as noted in Fig. 3, and the results of 1-butene conversion are shown in Fig. 4. In these experiments, the feed 1-butene could not be differentiated from the 1-butene produced by isomerization and/or by cracking. Therefore, from Fig. 4 of product distribution, 1-butene was eliminated. Although the introduction of this numerical ambiguity, the general trend of Fig. 4 consistently coincides with the results of propylene conversion shown in Fig. 3. Similar results were also obtained for other three butene isomers.

As we reported earlier⁹⁾, the rate of ethylene conversion is much lower than the rates of propylene and butenes conversions. Therefore, the reaction was carried out at 330°C which was higher by 30°C than that used for propylene and butenes conversions. The results are shown in Fig. 5. Even at 330°C, ethylene conversions on the Fe-silicates of Si/Fe 3,200 and 12 were only 51 and 4%, respectively; whereas on the H-ZSM-5's and Fe-silicates of Si/Fe 400 and 40, these catalysts substantially completed the conversion of ethylene. The result that the selectivity to aromatics and to light paraffins increased at higher reaction tem-

Feed gas, 100% 1-butene; temperature, 300°C; SV, 1,000 h⁻¹

Fig. 4 Product Distribution in the 1-Butene Conversion on Fe-Silicates and H-ZSM-5's with Different Si/Metal Ratios

Feed gas, 100% ethylene; temperature, 330°C;
SV, 1,000 h⁻¹

Fig. 5 Product Distribution in the Ethylene Conversion on Fe-Silicates and H-ZSM-5's with Different Si/Metal Ratios

Feed gas, 100% Propylene; SV, 1,000 h⁻¹

Fig. 6 Effect of Temperature on the Product Distribution in the Propylene Conversion on the Fe-Silicate Having Si/Fe Ratio 3,200

peratures on the H-ZSM-5's is a specific trend indicated by H-ZSM-5's. In the case of the two active Fe-silicates, their selectivities to aromatics and light paraffins were lower than those of the H-ZSM-5's. In other words, the specific catalytic properties of H-ZSM-5 and Fe-silicate which appeared in the propylene and butenes conversions exerted more specifically in the ethylene conversion.

3.4 Performance of the Fe-Silicate for Propylene Conversion under Various Reaction Conditions

Using the Fe-silicate of Si/Fe ratio 3,200, the

Feed gas, 17% propylene; SV, 900 h⁻¹

Fig. 7 Effect of Temperature on the Product Distribution in the Propylene Conversion on a Typical H-ZSM-5

effect of temperature on the product distribution was tested. In the whole temperature range tested, the propylene conversion was more than 96%. The hydrocarbon distribution obtained at each temperature is plotted in Fig. 6. To compare it with the result of a typical H-ZSM-5, the propylene conversion on H-ZSM-5 of Si/Al ratio 40 is shown in Fig. 7. The reaction conditions were the same as those of Fig. 6. At the reaction temperatures of 290 and 325°C, the Fe-silicate converted propylene to liquid products almost completely. The contents of aromatics and light paraffins were very low and, even at 360°C, these products increased but slightly. On the other hand, the H-ZSM-5 yielded considerable amounts of aromatics and light paraffins which increased with increasing temperature. The selectivity to C₁-C₄ paraffins of the H-ZSM-5 was 6.2 times that of the Fe-silicate at 360°C.

In Fig. 8, the effect of propylene concentration in the propylene conversion on the Fe-silicate is shown. The propylene concentration was allowed to vary from 27 to 100%, using N₂ as the diluent. The total space velocity of the gas mixture was maintained at 900 h⁻¹. Irrespective of the propylene concentration, almost a complete conversion of propylene was achieved. The selectivity to C₁-C₄ paraffins was almost always small. The C₅⁺ hydrocarbons, which consisted mainly of olefins, as will be mentioned later, increased remarkably with increasing propylene concentration from 27 to

Catalyst, Fe-silicate having Si/Fe ratio 3,200;
Temperature, 295°C; Diluent of propylene,
N₂; SV, 900 h⁻¹

Fig. 8 Effect of Propylene Concentration on the Product Distribution in the Propylene Conversion

53%, and above that concentration, the gasoline fraction attained ca. 87% even when the dissolved butenes (ca. 10%) was not taken into account.

The effect of space velocity (SV) on the propylene conversion on the Fe-silicate was then observed. The results are shown in **Figs. 9 and 10**. Surprisingly, the propylene fed had almost completely converted to liquid hydrocarbons even at such SV as high as 4,500 h⁻¹; the space-time conversion (STC) was 8.09 kg per liter catalyst per hour. Although the gasoline fraction (C₅-C₁₁) in the liquid product decreased with increasing SV (**Figs. 9 and 10**), this decrease was due to the increase in butenes as the selectivity to light paraffins remained small for all SV's. The extraordinary high space-time conversion of propylene or space-time yield (STY) of gasoline fraction indicates that diffusion resistance of this catalyst is very low, and there is no retardation by such phenomena as coke formation and strong adsorption of high molecular hydrocarbons in the vicinity of active sites. The absence of retardation is consistent with the weaker acidity of Fe-silicate than that of H-ZSM-5, while the rapid diffusion may be due to (1) the fine crystal size (0.5–1 μm) and (2) the presence of silica-rich layers at the outer surface of Fe-silicate crystal to decrease the coke formation at the outer surface layers.¹⁴⁾ The rapid diffusion is also favorable for decreasing the formation of light paraffins, because

Catalyst, Fe-silicate having Si/Fe ratio 3,200
Feed gas, 100% propylene; temperature, 300°C

Fig. 9 Effect of Space Velocity on the Space Time Conversion of Propylene and the Space Time Yield of Gasoline Fraction

Catalyst and reaction conditions are same as
Fig. 9

Fig. 10 Effect of Space Velocity on the Product Distribution in the Propylene Conversion

the olefins produced can be desorbed easily from the crystal to decrease the consecutive reaction to light paraffins and aromatics.

3.5 Catalyst Life Test

Tests on catalyst life over the Fe-silicate of Si/Fe ratio 3,200 was carried out 100 h on stream. The high propylene conversion was maintained throughout the test without any change. In the first 30 h, butane and aromatics decreased and after that period, the product distribution was consistently maintained. Although the light brown color of fresh catalyst changed slightly to yellowish brown

Table 1 Olefin/Paraffin Ratio in the Product Hydrocarbon for the Propylene Conversion on the Fe-Silicate

Hydrocarbon	Reaction Temperature (°C)		
	290	325	360
C ₂	24.8	38.6	38.3
C ₄	23.8	5.3	2.0
C ₅	15.2	7.5	2.4
C ₆	4.6	2.8	1.3
C ₇	2.1	3.0	1.7

Catalyst : Fe-silicate having Si/Fe 3,200

Feed gas : 100% propylene, SV : 1,000 h⁻¹

Table 2 Distribution of C₅ Olefins in the Product for the Propylene Conversion on the Fe-Silicate

Olefin	Reaction temperature (°C)		
	290	325	360
3-Methyl-1-butene	1.3%	1.8%	2.4%
1-Pentene	2.9	2.2	3.0
2-Methyl-1-butene	14.1	18.4	20.1
<i>trans</i> -2-Pentene	18.8	12.3	13.2
<i>cis</i> -2-Pentene	8.2	5.7	6.5
2-Methyl-2-butene	54.6	59.6	54.8
Cyclopentene	0.1	0.0	0.0

Catalyst : Fe-silicate having Si/Fe ratio 3,200

Feed gas : 100% propylene, SV : 1,000 h⁻¹

during the first 30 h, further change in color was not observed. This indicates that in early periods of reaction, the relatively strong acid sites, which provide active sites for aromatization and hydrogenation of olefins are covered with the coke formed, but after that the weaker acid sites perform without any coke formation and realize long catalyst life at least of 100 h on stream.

3.6 Properties of the Product

The gasoline fraction produced by the propylene conversion on the Fe-silicate during the steady selectivity period had a research octane-number 95. The olefin/paraffin ratio for each carbon-number molecule in the product and the distribution of pentene isomers are presented in **Tables 1** and **2**, respectively. The content of aromatics, which contribute to upgrading the octane-number, was low. However, as can be seen from **Table 1**, the olefin/paraffin ratio is large for any carbon number; and from **Table 2**, it is obvious that branched internal-olefins which themselves have high octane-values and which contribute to the high octane-number of the gasoline fraction are predominantly produced.

3.7 Specific Feature of Light Olefin Conversion on the Fe-Silicate

Based on the above observations, the principal reaction schemes for light olefin conversion on the

Catalyst, Fe-silicate having Si/Fe ratio 3,200
Feed gas, 100% propylene; temperature, 300°C;
SV, 1,000 h⁻¹

Fig. 11 Catalyst Life Test for the Fe-Silicate

Fe-silicates, which have very low activities for the formation of light paraffins and aromatics, can be derived as follows.

1. Oligomerization:

2. Isomerization: The skeletal isomerization from *n*-olefins to *iso*-olefins and the double-bond isomerization from α -olefins to internal olefins.

3. Cracking: Cracking of oligomers to other olefins. Besides the above principal reactions, the following disproportionation reaction occurs concomitantly during early reaction times on stream.

4. Disproportionation:

On H-ZSM-5, reaction (4) occurs as a result of oligomerization of the light olefins. On Fe-silicate, on the other hand, reactions (1), (2), and (3) proceed selectively to give principally branched mono-internal olefins. Furthermore, there is almost no coke formation via fused-ring aromatics formation. This guarantees a long catalyst life, maintaining high activity and selectivity. Although the selectivity to liquid products for H-ZSM-5 increased considerably by decreasing the reaction temperature to 260°C (**Fig. 7**), the numerical value

was still lower than that for Fe-silicate. Furthermore, the decrease in reaction temperature led to a decrease in conversion (ca. 60% at 260°C) and in catalyst life, indicating that the excellent catalytic performance of Fe-silicate could not be realized by merely decreasing the reaction temperature on H-ZSM-5.

The Fe-silicate has been revealed to be highly effective for the conversion of light olefins to liquid products (butenes, C₅-C₁₁ aliphatics, and small amounts of aromatics). Since the gasoline fraction is considered to be composed of C₅-C₁₁ hydrocarbons, high selectivity to liquid products does not necessarily mean high selectivity to gasoline fraction. On the Fe-silicate, however, butenes could also be converted to liquid product as described above. Therefore, recirculation of butenes or increase in contact time on the Fe-silicate would lead almost to a complete conversion of light olefins to the gasoline fraction. Such high selectivity to the gasoline fraction cannot be expected on H-ZSM-5, on which light paraffins (C₁-C₄ paraffins) cannot be converted selectively to the gasoline fraction. It should also be noted that commercial gasolines often dissolve butenes in addition to C₅-C₁₁ hydrocarbons, especially in the winter season. Consequently, the present study clearly indicates the availability of the Fe-silicate for selective conversion of light olefins to high octane-number gasolines.

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要 旨

鉄シリケート触媒上での低級オレフィンから高オクタン価ガソリンの高選択的合成

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石油危機以降, 石油代替燃料への転換が進められ, 重質油の余剰傾向が強まったため, 重質油をより有効に利用する新しい技術の開発が重要となってきた。本研究は, 重質油の熱分解などにより生成するエチレン, プロピレン, ブテンなど低級オレフィンを高オクタン価ガソリンへ高選択的に変換する触媒の開発を目的として行われたものである。

触媒には, H-ZSM-5 の Al 成分を種々の金属成分に置き換えたペンタシル型細孔構造を持つメタロシリケート類を用いた。これらは, アルミニウム塩の替りに他の金属塩を用いてシリカ成分との混合ゲルを形成させてから, 著者らが開発した迅速水熱合成法によって合成した。反応には, 通常の常圧流通装置 (Fig. 1) を用いた。各種メタロシリケートの性能をプロピレン転化で比較した結果, Al (すなわち ZSM-5), Ga, V, Cr, Zr-シリケートは, 液状炭化水素のほか, ガス状の $C_1 \sim C_4$ パラフィンを約 20~25% の選択率で生成した (Fig. 2)。これに対し, Fe-シリケートは, 定量的に液状炭化水素を生成

し (Figs. 2, 3), また, 極めて高い転化速度を実現できた。すなわち, 300°C , $SV\ 4,500\ \text{h}^{-1}$ の条件で, プロピレン転化率 95.6%, 空時収量は実に $8.09\ \text{kg/l}\cdot\text{h}$ にも達した。Fe-シリケートはブテン類 (Fig. 4), エチレン (Fig. 5) のガソリンへの選択的転換にも高性能を発揮した。さらに, Fe-シリケート触媒は反応温度, オレフィン濃度, 空間速度 (SV) の広い範囲で高い反応速度とガソリン選択率を維持した (Figs. 6, 8, 9, 10)。対照的に, ZSM-5 の場合には, 反応温度の上昇に伴い, ガス状の $C_1 \sim C_4$ パラフィンの生成が顕著になり, ガソリン選択率は著しく低下した (Fig. 7)。なお, Fe-シリケート触媒により合成されたガソリンのオクタン価は 95 という高い値を示したが, これは生成炭化水素が主にイソモノ内部オレフィンから成るためである (Tables 1, 2)。反応生成物中にコーク生成の前駆物質となる芳香族炭化水素が少ないので, 活性低下は少ないと予想されたが, 事実, 少なくとも 100 時間反応を継続しても劣化の兆候は見られなかった (Fig. 11)。

Keywords

Ferrosilicate, Gasoline synthesis, Metallosilicate, Olefin conversion