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Effect of hydrocarbon compositions in the M85 fuel on catalytic conversion

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Abstract

To identify hydrocarbon components suitably blended in the M85 (Methanol: 85 vol%, Gasoline: 15 vol%) fuel while maintaining high emission control performance of the catalyst, the effects of various hydrocarbons on the methanol conversion efficiency were investigated. Saturated hydrocarbons having about 5–7 carbon atoms did not inhibit the methanol conversion efficiency. In contrast, unsaturated hydrocarbons and aromatic hydrocarbons inhibited the methanol conversion efficiency. It was concluded that low saturated hydrocarbons such as light-naphtha were suitable for hydrocarbons mixed with methanol fuel.

Keywords: Methanol; N-hexane; M85 fuel; Saturated hydrocarbons; Unsaturated hydrocarbons; Aromatic hydrocarbons

1. Introduction

The use of methanol as a fuel for diesel vehicles is attracting wider attention not only as a substitute for petroleum fuel but also as a means for reducing nitrogen oxide (NO_x) and particulate emissions [1]. M85 fuel is known to be effective for Otto-type methanol engines for improving cold startability and other benefits [2]. However, M85 fuel is not suitable for Diesel-type methanol engines because of the deterioration of the oxidation ability of catalysts due to the hydrocarbons in the M85 fuel under the low exhaust gas temperature.

Therefore, the purpose of this study is to clarify the hydrocarbon compositions in the M85 fuel which are able to achieve a high catalytic conversion efficiency under the low exhaust gas temperature.

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2. Experimental

The oxidation of methanol was tested by using a fixed-bed flow reactor. The tested catalyst (Pt/Rh= 5/1) was made by N.E. CHEMCAT. The tested gas was synthesized on the basis of actual exhaust gas compositions in idling of Diesel-type methanol engine. The tested gas consisted of carbon monoxide, oxygen, nitrogen oxide, water, methanol and various hydrocarbons. Test conditions and the tested gas composition ratio are shown in Table 1.

3. Results and discussion

Fig. 1 shows the catalyst temperature dependence of methanol and *n*-hexane conversions by *n*-hexane, methanol and a mixture of methanol and *n*-hexane. Methanol conversion efficiency in the case of methanol mixed with *n*-hexane is almost the same as that in

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Table 1
Test conditions

Catalyst	Pt–Rh/Al_2O_3
Space velocity	13 500 h^{-1} (101 kPa)
CO	1900 ppm
NO	1100 ppm
O_2	14.6%
HC	CH_3OH:HC=85:15 (vol%)
	CH_3OH 6400 ppm
	HC (except CH_3OH) about 2100 ppm
H_2O	11%

the case of only methanol. Namely, methanol conversion efficiency does not inhibit in the presence of hexane. In contrast, *n*-hexane conversion activity is decreased when *n*-hexane is blended in, as compared with the case where only *n*-hexane is used. Therefore, *n*-hexane conversion efficiency is inhibited in the presence of methanol. This is a typical tendency of the catalyst temperature dependence of methanol and hydrocarbons in the case of saturated hydrocarbons. It is considered that oxidation activity of methanol is higher than that of saturated hydrocarbons. So, absorbed oxygen in catalyst is mainly expended by oxidation reaction of methanol.

Fig. 2 shows the catalyst temperature dependence of methanol conversion in the case of various saturated hydrocarbons in the M85 fuel. Generally, in the case of saturated hydrocarbons having about 2–7 carbon atoms, there are no significant differences in the methanol conversion according to the kind of hydrocarbon.

Fig. 3 shows the catalyst temperature dependence of hydrocarbon conversion using synthetic gases containing various saturated hydrocarbons blended with methanol. As the carbon atoms in hydrocarbons increased, hydrocarbon conversions increased. Especially, conversion of saturated hydrocarbons having five or more carbon atoms increased under low catalyst temperature.

As a result shown in Figs. 2 and 3, it is found that saturated hydrocarbons having about 5–7 carbon atoms are suitable hydrocarbon components for blending with methanol.

Fig. 4 shows the catalyst temperature dependence of methanol and ethylene conversions by ethylene, methanol and a mixture of methanol and ethylene. Ethylene conversion efficiency in the case of ethylene mixed with methanol is almost the same as that in the case of only ethylene. Thus, ethylene conversion does not inhibit in the presence of methanol. On the other hand, methanol conversion activity in the case of only methanol is higher than that of methanol mixed with ethylene. Therefore, methanol conversion efficiency inhibits in the presence of ethylene. This is a typical tendency of the catalyst temperature dependence of methanol and hydrocarbons in the case of unsaturated hydrocarbons and aromatic hydrocarbons. It is considered that the oxidation activity of unsaturated

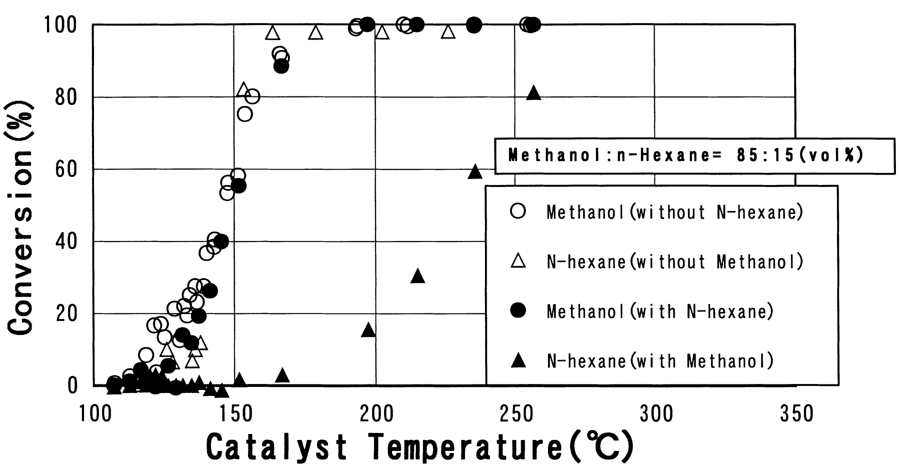

Fig. 1. Catalyst temperature dependence of *n*-hexane and methanol conversions.

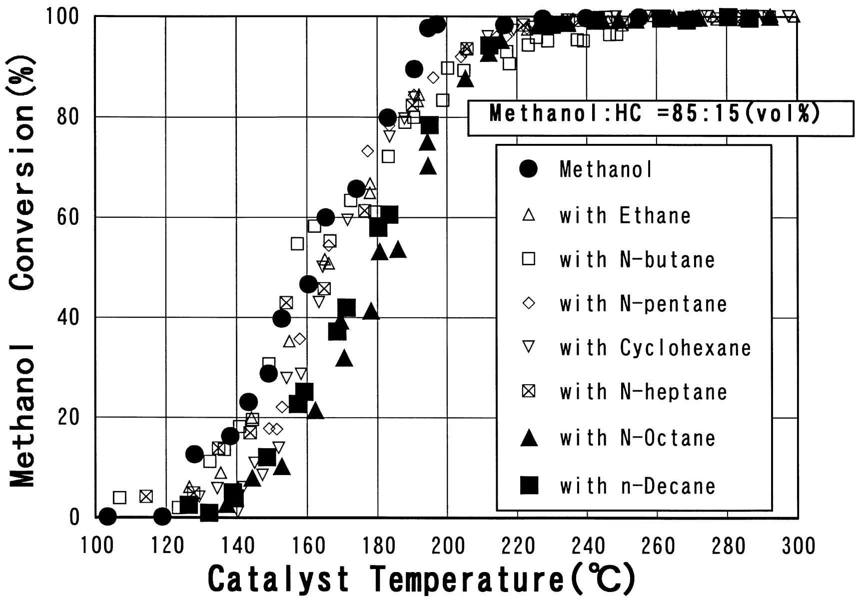

Fig. 2. Effect of various saturated hydrocarbons on methanol conversion.

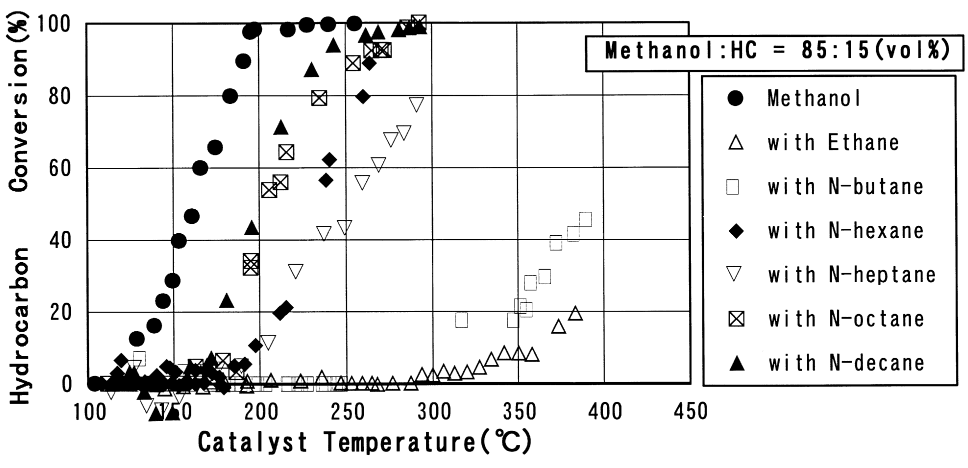

Fig. 3. Saturated hydrocarbon conversion in M85 fuel.

hydrocarbons and aromatic hydrocarbons are higher than that of methanol. So, absorbed oxygen in catalyst is mainly expended by oxidation reaction of unsaturated hydrocarbons and aromatic hydrocarbon.

Fig. 5 shows the effect of unsaturated hydrocarbons in the M85 fuel on methanol conversion. Unsaturated hydrocarbons inhibit the methanol conversion efficiency. As the carbon atoms in hydrocarbons increase, methanol conversion decreases.

Fig. 6 shows the catalyst temperature dependence of various unsaturated hydrocarbon conversion in the M85 fuel. As the carbon atoms in hydrocarbons increased, hydrocarbon conversions decreased.

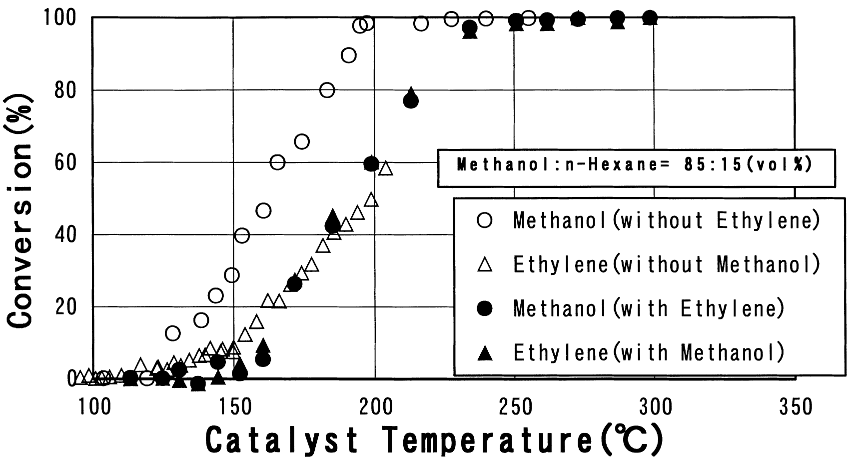

Fig. 4. Catalyst temperature dependence of ethylene and methanol conversions.

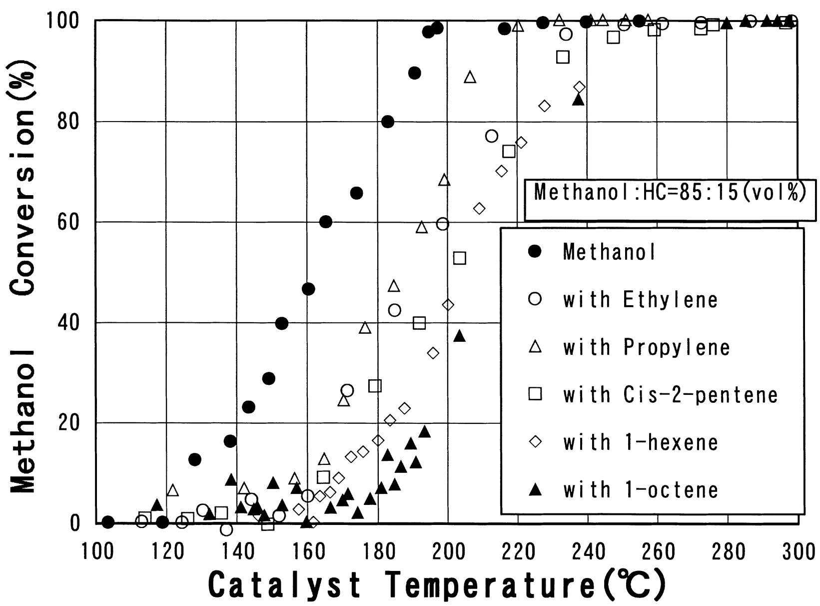

Fig. 5. Effect of various unsaturated hydrocarbons on methanol conversion.

Fig. 7 shows the relationship of methanol decay ratio and toluene concentration in the case of a mixture of methanol and toluene under several catalyst temperatures. The methanol decay ratio is determined from the ratio of methanol conversion in the pure methanol fuel (M100) to methanol conversion in each toluene concentration. As the toluene concentration increases, methanol decay ratio decreases. Furthermore, as the catalyst temperatures become lower, the methanol decay ratio decreases.

Fig. 8 shows the catalyst temperature dependence of methanol conversions by gasoline and light-naphtha mixed with methanol. Methanol conversion

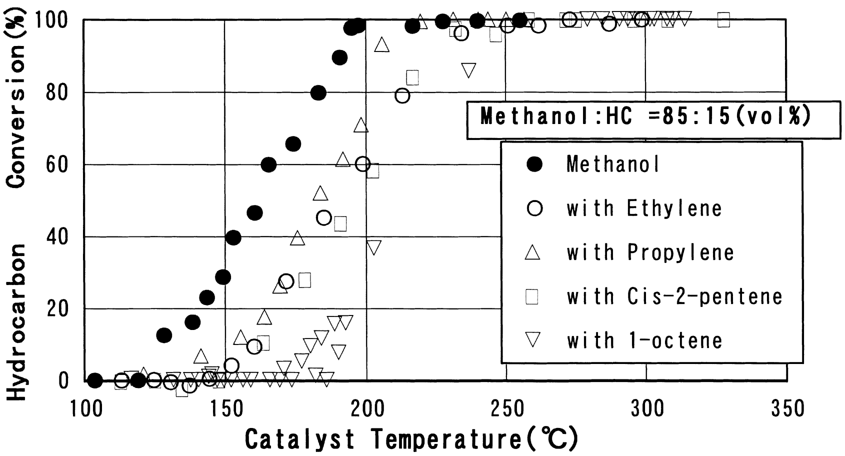

Fig. 6. Unsaturated hydrocarbon conversion in M85 fuel.

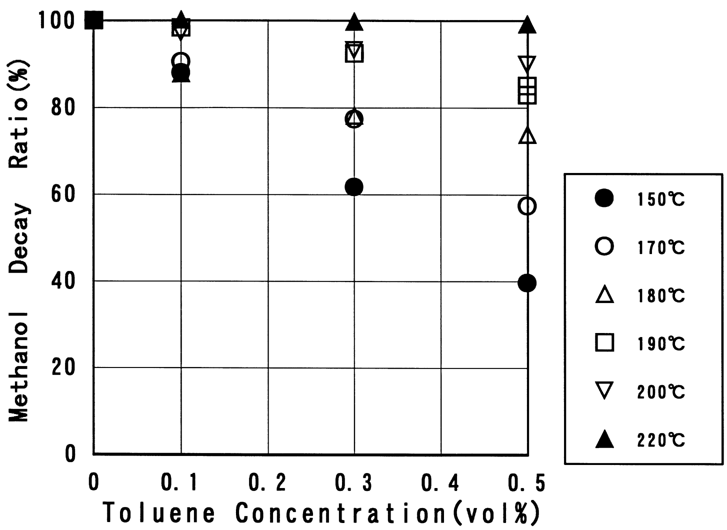

Fig. 7. The dependence of methanol reduction rate on toluene concentration under several catalyst temperatures.

is not inhibited in the presence of light-naphtha. However, methanol conversion inhibits in the presence of gasoline.

4. Conclusion

It is concluded that saturated hydrocarbons containing about 5–7 carbon atoms are suitable hydrocarbon components for blending with methanol because of their superior conversion characteristics in not impairing the catalytic activity for oxidizing methanol. On the other hand, unsaturated hydrocarbons and aromatic hydrocarbons are found to be unsuitable due to their adverse effects on the catalytic activity for oxidizing methanol.

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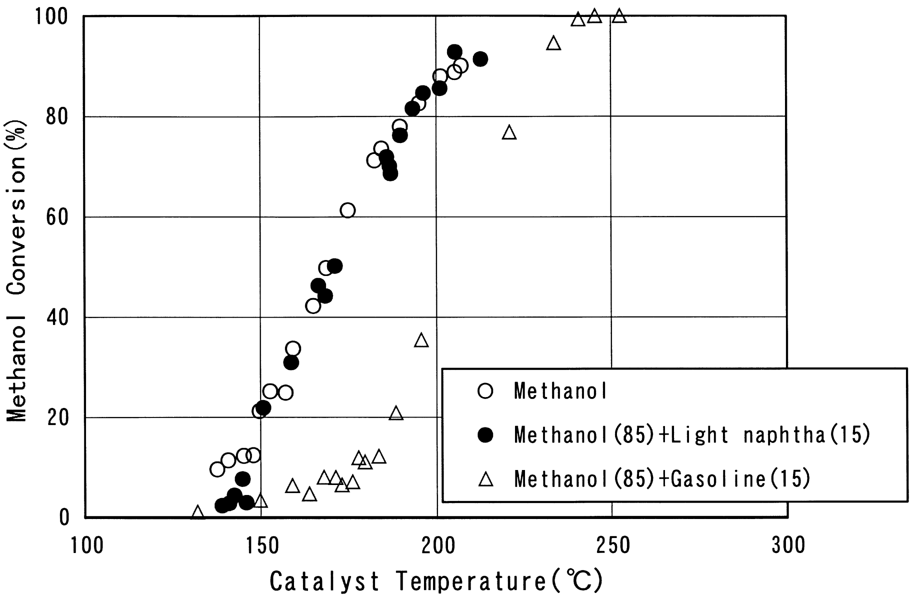

Fig. 8. Dependence of methanol conversions by gasoline and light-naphtha with methanol.

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