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Hydrogenation of Carbon Monoxide over the Mixed Catalyst Composed of Co-Ni/MnO-ZrO_2 and Zeolite Catalyst

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The mechanical mixtures of Co-Ni/MnO-ZrO_2 and zeolite were used as catalysts for the selective synthesis of gasoline by CO hydrogenation. Formation of branched-paraffins was promoted but that of higher hydrocarbons than carbon number of 10 was suppressed by combination with zeolite. The product distribution strongly depended on the type of zeolite catalyst. The combination of Co-Ni/MnO-ZrO_2 with PtH-pentasil zeolite was very active for the formation of gasoline with high octane number.

A variety of products with different carbon number is generally obtained in CO hydrogenation over Fischer-Tropsch catalysts. One of the important aims in this reaction is the control of products, in particular, to enhance the selectivity to gasoline. Metal-zeolite catalysts have been employed for reforming the CO hydrogenation products to the desirable products.[1-3] But the yield of gasoline on the conventional metal-zeolite catalysts is not satisfactory due to a low activity of Fischer-Tropsch catalyst. We have reported that Co-Ni alloy catalyst supported on MnO-ZrO_2 is very active for the production of gasoline. But the octane number of produced gasoline on this catalyst is low. Moreover, the yield of gasoline is not satisfactory because of the high selectivity to higher hydrocarbons and CH_4. High octane number can be attained by increasing the content of branched-paraffins. Zeolite catalyst is highly active for reforming and cracking reaction. Combination of zeolite with Co-Ni/MnO-ZrO_2 leads to the selective catalyst for gasoline synthesis. In this study, the combination effect of the Co-Ni/MnO-ZrO_2 and zeolite catalysts was investigated for enhancing the yield of gasoline and its octane number.

The MnO-ZrO_2 support was prepared by coprecipitation of metal nitrates.[4] The alloy catalyst of 50Co50Ni/50MnO50ZrO_2, which is expressed hereafter as Co-Ni/MnO-ZrO_2, was prepared by the incipient wetness technique by the previous method.[4] Zeolite catalysts (Tosoh Mfg. Co. Ltd.) were mixed with the same weight of Co-Ni/MnO-ZrO_2 after ion-exchange with H, Na, or Pt. Hydrogenation was performed at 523 K, 1.0 MPa. A gaseous mixture of H_2 (64 vol%), CO (32 vol%), and Ar(4 vol%) was fed to the catalyst bed at W/F=20 g-cat.h/mol (where F is the flow rate of reactants and W is the weight of Co-Ni/MnO-ZrO_2 and zeolite). The research octane number was estimated from the product selectivities.

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Zeolite catalyst was combined with F-T catalyst by two methods. The mixture of two catalysts pellets was placed as one catalyst bed in method B and two catalyst beds were placed in series in one reactor in method A , i.e., the reaction gas passing through the Co-Ni/MnO-ZrO_2 bed was fed into the zeolite bed. The overall CO conversion decreased slightly in method A as shown in Fig. 1. The formation of higher hydrocarbons than carbon number of 12 was not recognized in the effluent gas. On the other hand, method B was more effective in producing branched-paraffins and suppressing the formation of hydrocarbons higher than carbon number of 13. The octane number of gasoline produced on the Co-Ni/MnO-ZrO_2 catalyst was only 11, while that became 64 and 74 in methods A and B, respectively. In the following part of

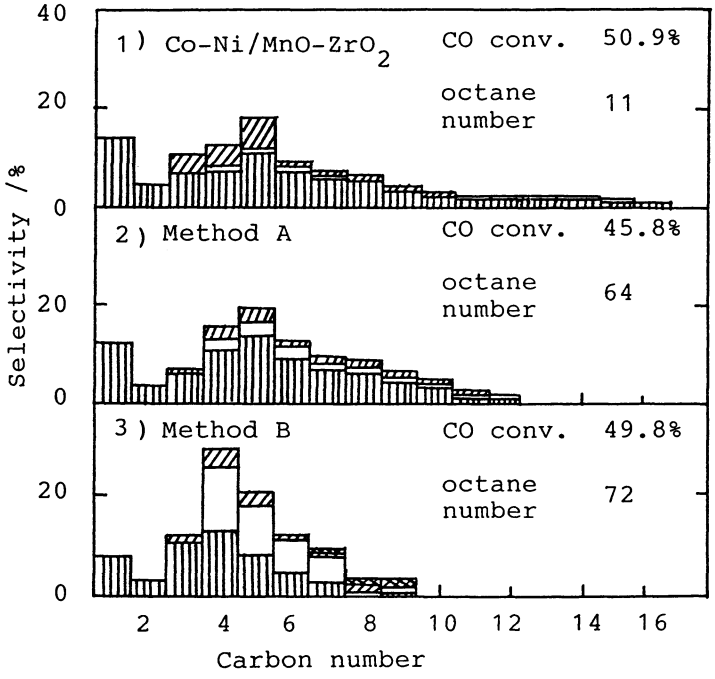

Fig. 1. CO hydrogenation over Co-Ni/MnO-ZrO_2 combined with H-pentasil zeolite.
n-paraffins i-paraffins
olefins aromatic hydrocarbons

Table 1. CO hydrogenation over Co-Ni/MnO-ZrO_2 combining with zeolite catalysts

Zeolite	Al cont.	CO conv.	Selectivity/% [a]							Octane
	mmol g^{-1}	%	CH_4	C_2^--C_4^-	$C_2^=$-$C_4^=$	C_5-C_{11}	C_{12+}	Arom.	Oxy.	number
None		50.9	13.9	17.3	8.9	48.7	9.8	0	1.4	11
Na-Pentasil	1.32	21.6	21.1	19.0	17.7	37.2	1.8	1.6	1.6	47
Na-Mordenite	2.73	28.6	21.6	22.2	13.0	39.2	2.5	0	1.5	20
Na-Ferrierite	1.77	24.4	25.4	23.2	16.7	33.1	1.4	0	0.1	37
Na-O/E[b]	3.54	24.1	24.7	23.4	14.6	35.2	2.1	0	0.2	24
H-Pentasil	1.32	49.8	7.4	38.6	5.2	45.5	0	2.4	1.0	72
H-Mordenite	2.73	30.4	21.9	21.4	14.9	38.3	1.5	1.7	0.5	50
H-Ferrierite	1.77	19.6	21.9	23.0	16.5	35.1	1.7	1.6	0.2	59
H-O/E[b]	3.54	15.5	26.2	20.4	16.0	34.9	1.9	0	0.6	49
PtH-Pentasil[c]	1.32	52.8	6.8	38.9	2.9	44.5	0	4.9	2.0	75

a) Calculation based on the carbon number. b) Offretite/Erionite.
c) Pt loading is 0.5 wt%.
523 K, 1.0 MPa, H_2/CO=2.0, W/F=20 g-cat.h/mol, Zeolite/Co-Ni/MnO-ZrO_2=1
Al cont.: Al content of zeolite, C_2^--C_4^-: C_2-C_4 paraffins, $C_2^=$-$C_4^=$: C_2-C_4 olefins, C_5-C_{11}: gasoline fraction, C_{12+}: higher hydrocarbon than carbon number of 11, Arom.:Aromatic hydrocarbons, Oxy.: oxygenated compounds,
Octane number:research octane number of gasoline fraction

this study, we tried the CO hydrogenation over the mechanical mixture catalyst in method B because of the high yield of gasoline and high octane number.

Table 1 summarizes the dependence of activities and selectivities on the types of zeolite mixed with Co-Ni/MnO-ZrO_2. In this table, hydrocarbon products are grouped into seven categories, CH_4, C_2-C_4 olefins, C_2-C_4 paraffins, C_5-C_{11}, hydrocarbons higher than carbon number of 11 (C_{12}^+), aromatics, and oxygenated compounds. A small amount of alcohols was sometimes produced as oxygenated compounds. Combination with zeolite generally lowered the overall CO conversion except for H- or PtH-pentasil. The selectivity to branched-paraffins, especially to C_4 and C_5, always increased, but the formation of higher hydrocarbons than carbon number of 11 was suppressed. Proton-exchange was generally more active than Na-type zeolite for the formation of branched-paraffins. Pentasil-type zeolite was the most active for the formation of branched-paraffins, but inactive for olefin formation. The formation of branched-paraffins was further promoted by Pt ion-exchanging pentasil-type zeolite. Pt ion-exchange also promoted the production of aromatics from lower paraffins.[6] Since the product selectivity strongly depended on the kind of zeolite catalyst in Table 1, the reactivity of zeolite catalyst for higher hydrocarbons appears to have a decisive role in the product distribution on these mixed catalyst.

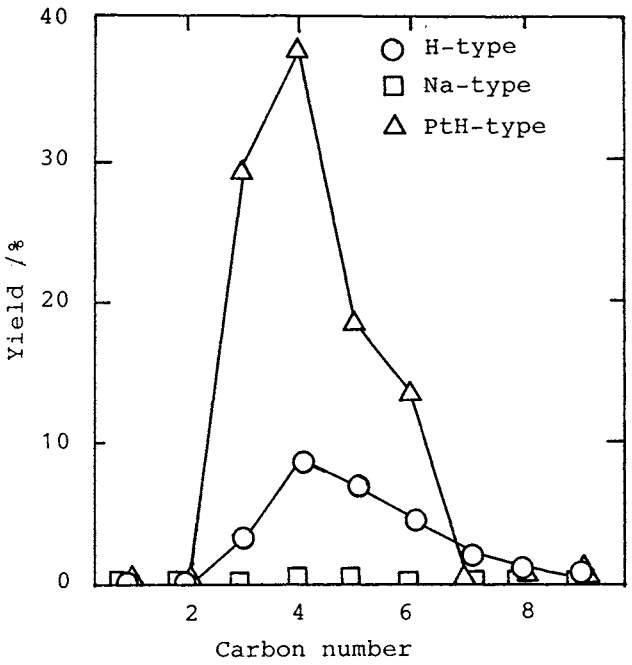

Fig. 2. Hydrogenolysis of n-decane over pentasil zeolite. (523 K, 0.1 MPa, $H_2/n\text{-}C_{10}$=15, W/F=10 g-cat.h/mol)

The hydrogenolysis of n-decane was studied as a model reaction over H-, Na-, and PtH-pentasil type zeolite in Fig. 2. PtH-pentasil was the most active for the hydrogenolysis, but Na-pentasil zeolite was inactive. The high selectivity to i-C_4 in CO hydrogenation over Co-Ni/MnO-ZrO_2 with H-pentasil catalysts results from hydrogenolysis reaction of higher hydrocarbons on zeolite catalyst. Since the hydrogenolysis of higher hydrocarbons proceeds on the Bronsted acid sites,[7] the selectivity to branched-paraffins becomes higher on the catalyst combined with H- and PtH-types than Na-type zeolite.

Temperature dependence of catalytic activity and selectivity was investigated using the Co-Ni/MnO-ZrO_2 mixed with PtH-zeolite in Fig. 3. At elevated temperatures, the CO conversion and selectivities to branched-paraffins and CH_4 increased, but the selectivities to gasoline and olefin lowered. The octane number of gasoline was maximum (93) at 573 K because the formation of branched-paraffins was promoted. At 543 K, the CO conversion became 85.8%, which was 8 times higher than that of 503 K and the formation rate of gasoline

attained maximum (1.71×10^{-4} $molmin^{-1}g^{-1}$). Moreover, the C_2-C_4 paraffins produced on this mixed catalyst mainly consisted of i-C_4, thus the yield to higher hydrocarbons than carbon number of 3 was as high as 54% at 543 K. These catalysts far exceeded the commercialized Synthol ones in the yield of gasoline and its octane number.[8] The conversion of CO attained 100% at 573 K, while the methanation proceeded dominantly. Although reforming activity over pentasil zeolite is the highest at 803 K,[6] methanation proceeds mainly on Co-Ni/MnO-ZrO_2 at such a high temperature.[4] Therefore, the optimum temperature for gasoline synthesis on these two beds catalyst was ca. 543 K.

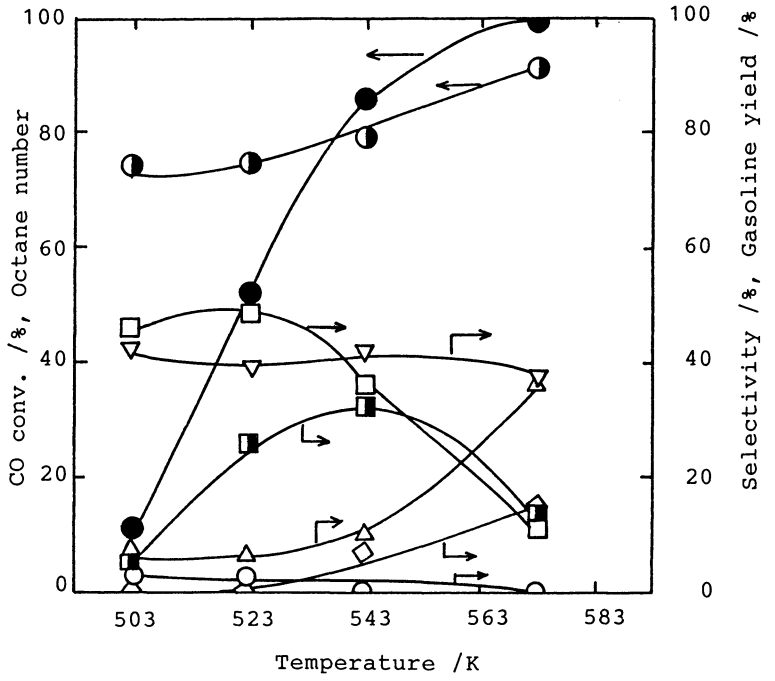

Fig. 3. Temperature dependence of catalytic activity and selectivity in CO hydrogenation over Co-Ni/MnO-ZrO_2 mixing with PtH-pentasil.
● CO conversion △ CH_4 ▽ C_2-C_4 paraffin
○ C_2-C_4 olefin □ gasoline ◇ CO_2
◑ reserch octane number ◨ gasoline yield

The product distribution in CO hydrogenation can be controlled by combination of Co-Ni/MnO-ZrO_2 with zeolite catalyst. Since the reforming reaction requires the trong acid sites, pentasil zeolite, which possesses the large amount of strong acid sites, is adequate for enhancing the formation of branched-paraffins.[9] The mixture of Co-Ni/MnO-ZrO_2 and PtH-pentasil pellets is one of the promised catalysts to selectively synthesize the gasoline with high octane number by CO hydrogenation.

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