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Reaction Mechanism for Selective Synthesis of Gasoline-Range Isoalkanes from Syngas over RuPtHY Zeolites. II.[1) Role of Metals and Acid Sites

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Role of metals and acid site in selective synthesis of gasoline-range isoalkanes from syngas catalyzed by zeolite Y supported Ru–Pt alloy has been studied. As a probe molecule 1-alkene was added into syngas over the various combination of catalysts. Alloying Ru with Pt enhanced 1-octene conversion as well as CO conversion. Reaction of 1-octene over metal-free DAHY (dealuminated HY) zeolite produced cracking products with high selectivity for isobutanes; C_{3+} carbon number distribution was similar to that from CO hydrogenation over DAHY2R2P (Ru and Pt 2 wt%, respectively), suggesting that the selective formation of isoalkanes in gasoline-range from CO–H_2 over DAHY2R2P could be essentially due to acid-catalyzed reactions on zeolites. Cracking of 1-octene was affected by the support and increased in the order: NaY2R2P<HY2R2P<DAHY2R2P. Products via disproportionation were predominant for NaY2R2P and HY2R2P and those via simple cracking prevailed in DAHY2R2P. This could account for shift to light side in carbon number distribution from simple CO hydrogenation over DAHY2R2P. From syngas H_2/CO ratio= 13/2, methane was the main product. However, methane production was virtually unchanged on addition of 1-octene, implying that the presence of CO suppressed the hydrogenolysis of 1-octene on RuPt bimetallic site. Effects of contact time and temperature on selectivity for products were also discussed.

Non-Schulz–Flory kinetics in Fischer–Tropsch synthesis has been studied by several authors.2–8) Limitation on chain growth has been reported for RuNaY,2) RuLaY,3) FeNaY,4) RuPtHY,5) and Co-alumina6) catalysts. With Co–alumina, a maximum in carbon number distribution was dependent on the pore size of the support. Over the ruthenium-encaged NaY or LaY zeolite, the product contained no hydrocarbons larger than C_{11}; the chain growth probability suddenly dropped as chain length increased. This product pattern was ascribed to particle size effect of the ruthenium metals in zeolite.7)

In a previous paper, we reported the selective synthesis of gasoline-range products rich in isoalkanes over RuPt-HY or DAHY (dealuminated HY).5) The deviation from the Schulz–Flory product pattern was attributed to secondary reactions rather than the effect of particle size,7) since increasing the ruthenium particle size in HY had no effect on final products pattern.5) The evidence for secondary reactions was obtained by adding 1-alkenes (C_n) in the range of C_3—C_{11} as probe molecules into synthesis gas.1) Addition of light alkenes (n=3,4) resulted in a pronounced increase in the yield of C_{n+1} and heavier, which could be ascribed to the oligomerization of feed alkene followed by cracking. On the other hand, simple cracking predominated in the case of addition of heavy alkenes ($n \geq 7$).

In the present paper, we report a study of the role of acid sites and Ru–Pt bimetallic sites in the selective formation of gasoline-range isoalkanes from synthesis gas. The dependence of H_2/CO ratio, contact time and temperature on the product selectivity is also discussed from mechanistic viewpoints.

Experimental

Catalysts were prepared by simultaneous ion exchange with an aqueous solution containing $[Ru(NH_3)_6]Cl_3$ and $[Pt(NH_3)_4]Cl_2$, as described previously.5) NaY (SiO_2/Al_2O_3= 4.8) was obtained from Nikka Seiko Co. HY was prepared by ion exchange of NaY with an aqueous solution of NH_4NO_3, followed by calcination at 400 °C. DAHY (dealuminated HY, SiO_2/Al_2O_3=7.6) was obtained from Shokubai Kasei Co. The designation of catalyst is, for example, DAHY2R2P which stands for a catalyst with 2% Ru and 2% Pt by weight supported on DAHY. Reaction was carried out with a continuous flow tubular reactor containing 1 g of catalyst. The standard reaction conditions were 240 °C, 1.5 MPa, H_2/CO=3/2, and W/F=12.5 g-cat. h mol.$^{-1}$ Liquid alkene was added by use of a high pressure microfeeder and homogeneously mixed with synthesis gas over the preheated quartz wool-packed bed before the reaction zone. Detailed analysis of hydrocarbon products was carried out on a gas chromatograph equipped with a chemically bonded OV-1 capillary column. Each product was identified with a Shimadzu QP-1000 mass spectrometer. Chemisorption of NH_3 was carried out by using a grease-free glass constant-volume adsorption system. The sample was evacuated at ambient temperature and then subjected to temperature-programmed desorption (TPD) analysis of NH_3. The heating rate was 7 °C min^{-1} and the amount of NH_3 was determined mass spectrometrically.

Results and Discussion

Effect of Metal Loadings. The catalyst activity substantially declined during the course of a catalytic run. Figure 1 shows the change of CO conversion with time on stream over DAHY2R and DAHY2R2P in the absence and presence of 1-octene. Deactivation proceeded faster in the presence of 1-octene than in its

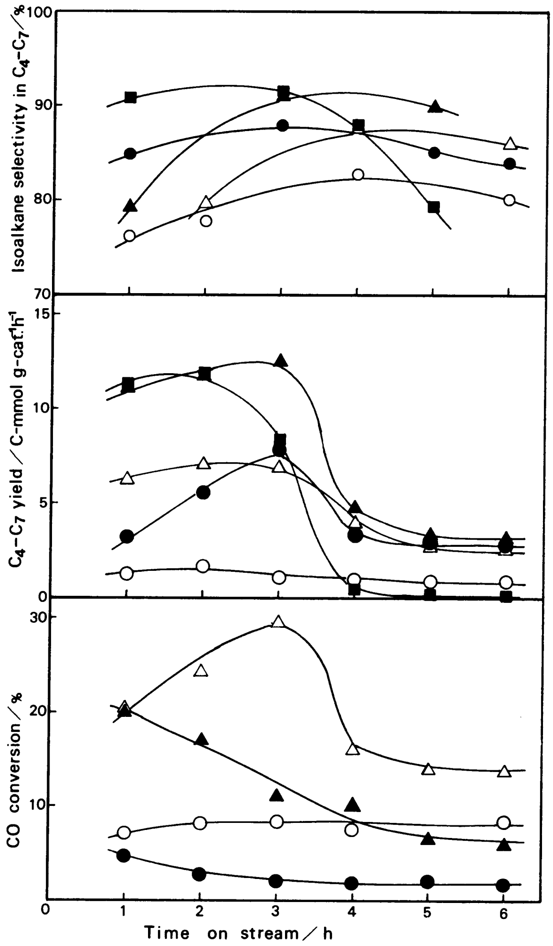

Fig. 1. Change of catalytic performance with time on stream. Reaction conditions: 240 °C, 1.5 MPa, $H_2/CO=3/2$, W/F=12.5 g-cat. h mol^{-1}, 1-octene feed rate=1.9 mmol g-cat.$^{-1}$ h^{-1}. Simple CO hydrogenation: △, DAHY2R2P; ○, DAHY2R. 1-Octene addition: ▲, DAHY2R2P; ●, DAHY2R; ■, DAHY (under He).

absence. In view of previous work,[8] this could be interpreted in terms of acceleration of coke deposition. Alloying of Ru with Pt enhanced CO conversion,as was observed with the HY-supported catalysts.[5] This was also the case in the presence of 1-octene.

The changes of the yield of and the isoalkane selectivity for C_4—C_7 fraction with time on stream are also shown in Fig 1. The effect of metal loadings on products is summarized in Table 1, where data obtained after 2—3 h on stream are adopted. The addition of 1-octene resulted in an increase in the yield of C_4—C_7, associated with the increase in their *i/n* ratios. Products in the C_4^+ range consisted mostly of branched alkanes. Alkanes with quaternary C-atoms were negligible for all the catalysts.[1,5] In most cases the fractions of monobranched alkanes in the range of C_4—C_6 were far above the equilibrium. Higher-than-equilibrium *i/n* ratios of C_4 and C_5 should be taken as evidence for the occurrence of carbenium ion cracking process.[1,9]

DAHY2R2P was similar to DAHY2R in the carbon number distribution of the products from CO-H_2 except for slightly increased selectivity for C_4—C_7.[5] The apparent conversion of 1-octene was considerably higher over DAHY2R2P than over DAHY2R. This higher cracking activity might be the cause of higher *i/n* ratios of C_4 and C_5 in simple CO hydrogenation over DAHY2R2P.[1] DAHY2P showed prolonged cracking activity of 1-octene than the other cases.

Cracking behavior of 1-octene under He flow over metal-free DAHY was also investigated. High initial selectivity for C_4 and no appreciable formation of C_1 and C_2 were observed, as would be expected for the acid-catalyzed cracking. As shown in Table 1, there were similarities between simple CO hydrogenation over DAHY2R2P and 1-octene cracking over DAHY in C_3^+ products distribution and selective formation of isoalkanes. Thus the selective formation of isoalkanes in gasoline-range from CO-H_2 over DAHY2R2P could be essentially due to acid-catalyzed reactions on zeolites. It should be noted that the metal-free DAHY support gave products exceptionally rich in branched isomers in C_4 and C_5 fractions, especially in the initial stage of the reaction. This could be caused by an increase in lifetime of carbenium ions associated with a low reactivity of hydrogen in the absence of metals,[10,11] resulting in the increased probability of isomerization before desorbing. The presence of metallic components should promote the hydrogenation of alkene to alkane and also may enhance hydrogen spillover to acid site,[12,13] leading to the formation of more normal isomers. In this regard, the proximity of metal and acid sites should be important to balancing these two functions.[5] On metal-free DAHY, decay of acid catalyzed cracking proceeded fast (Fig. 1) and the recovery of 1-octene added was ca. 60% after 2—3 h on stream, which suggested significant coke deposition.[8]

Effect of Support. Carbon number distribution of the products from CO-H_2 reaction was shifted to light side in the order: NaY2R2P[14,15]<HY2R2P<DAHY2R2P.[5] When 1-octene was added to syngas, product distribution was affected by concurrent cracking of 1-octene; apparent conversion[1] of 1-octene after 2—3 h on stream increased in the order: NaY2R2P (15%)< HY2R2P (26%)<DAHY2R2P (65%). As a result, yield of C_3—C_7 hydrocarbons increased by 1-octene addition in the same order: NaY2R2P<HY2R2P<DAHY2R2P.

TPD (temperature-programmed desorption) measurement of NH_3 revealed that the amounts of weak and strong acid, defined as the amount of ammonia desorbed below and above 350 °C, respectively, were as follows: NaY2R2P (1.51/0.20 mmol g-cat.$^{-1}$), HY2R2P (4.17/0.43 mmol g-cat.$^{-1}$), and DAHY2R2P (3.42/0.68 mmol g-cat.$^{-1}$). Therefore, the cracking tendency of 1-octene could be related to the amount of strong acid

Table 1. Effect of Metallic Composition on 1-Octene Cracking[a)]

Catalyst	DAHY2P	DAHY2R		DAHY2R2P		DAHY
Additive	1-Octene	None	1-Octene	None	1-Octene	1-Octene
CO conv./%	0.0	5.8	5.0	27.5	17.1	—
1-Octene Conv./%	97.3	—	42.1	—	65.0	95.7
Carbon number	Distribution/mmol g-cat.$^{-1}$ h^{-1}					
C_1	0.17	0.19	0.28	0.56	0.78	0.00
C_2	0.01	0.00	0.06	0.05	0.10	0.00
C_3	0.33	0.06	0.21	0.26	0.28	0.17
C_4	2.05	0.12	0.77	0.54	1.27	1.05
C_5	0.84	0.09	0.40	0.38	0.72	0.50
C_6	0.25	0.06	0.23	0.23	0.36	0.23
C_7	0.03	0.03	0.17	0.14	0.29	0.08
C_8	0.02	0.01	1.08	0.08	0.66	0.07
C_9	0.00	0.00	0.02	0.04	0.04	0.01
C_{10}	0.00	0.00	0.00	0.02	0.02	0.01
C_{11}	0.00	0.00	0.00	0.00	0.01	0.00
C_{12}^+	0.02	0.00	0.00	0.00	0.01	0.00
	i/*n* ratio (eq.[b)])					
C_4(1.1)	7.1	3.4	3.7	3.8	4.6	10.4
C_5(4.0)	18.8	5.1	16.0	14.9	15.6	135.0
C_6(5.9)	8.7	6.2	3.4	11.3	18.5	9.5
C_7(9.7)	3.2	6.3	31.0	15.6	28.0	4.6
C_8(7.1)	1.5	3.8	8.3	10.0	11.2	0.3

a) Reaction conditions : 240°C, 1.5 MPa, W/F=12.5 g-cat. h mol^{-1}, $H_2/CO=3/2$, 1-octene feed rate=1.9 mmol g-cat.$^{-1}$h^{-1}, data obtained after 2—3 h on stream, 1-octene cracking over support under flow of He b) Thermodynamic equilibrium at 240°C.

sites on the catalysts: NaY2R2P<HY2R2P<DAHY2R2P. It is generally known that cracking requires strong acid sites.[16)] Selectivity for C_4 fraction and apparent 1-octene conversion are plotted against the amount of strong acid sites of the catalysts in Fig. 2. The content of isobutane amounted to more than 80% of C_4 fraction. The increase in isobutane should come from simple cracking of 1-octene following skeletal isomerization of carbenium ion on acid sites. This type of simple cracking was remarkable for DAHY2R2P, which possesses stronger acid sites than HY2R2P or NaY2R2P.

$$C_8 \rightarrow 2C_4 \tag{1}$$

The increase in the yield of C_7 and C_6 should originate from the disproportionation of feed 1-octene, since neither C_6 nor C_7 can be directly formed by β-scission of C_8 carbenium ions.

$$2C_8 \rightarrow [C_{16}]\left\langle\begin{array}{l}\nearrow C_7 + C_9\\ \searrow C_6 + C_{10}\end{array}\right. \tag{2}$$

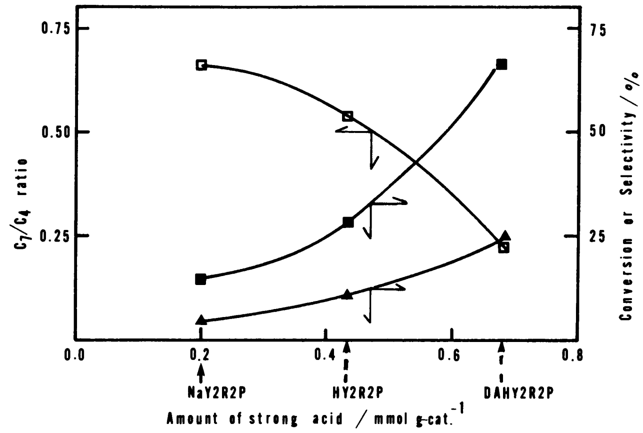

Fig. 2. 1-Octene conversion over NaY2R2P, HY2R2P, and DAHY2R2P. Reaction conditions: 240 °C, 1.5 MPa, $H_2/CO=3/2$, W/F=12.5 g-cat. h mol^{-1}, 1-octene feed rate=1.9 mmol g-cat.$^{-1}$ h^{-1}, after 2—3 h on stream. □, C_7/C_4 ratio; ■, 1-octene conversion;[1)] ▲, C_4 selectivity.

An attempt was made to estimate the contribution of the disproportionation and the simple cracking to the carbon number distribution. Based on the Eqs. 1 and 2, the ratio of C_7/C_4 was taken as a crude measure of the ratio of disproportionation to simple cracking and shown in Fig. 2. The C_7/C_4 ratio decreased in the order: NaY2R2P>HY2R2P>DAHY2R2P. This indicates low selectivity for disproportionation with the catalysts with a large amount of strong acid sites, as was proposed by Corma et al.[17)] Molar ratios of C_7/C_9 and C_6/C_{10} are much larger than unity, suggesting subsequent cracking of heavy disproportionation products. The disproportionation/cracking ratio was also dependent on chain length of feed alkenes. With DAHY2R2P the ratio increased with decreasing the chain length as follows: $C_8<C_7<C_6$.[1]

Isomer distribution of C_8 fractions was scarcely dependent on the support, as shown in Fig. 3. The remaining C_8 feed consisted mostly of monobranched alkanes and dibranched alkanes. This suggests that relatively strong acid sites are not required for skeletal isomerization.[18] Cracking of alkanes and alkenes on large pore zeolite is considered to be preceded by conversion to readily formed branched isomers. With all this, it could be understood that the reaction path of 1-alkene should be strongly dependent on the acid properties of supports. The observed shift to the light side in carbon number distribution from simple CO hydrogenation over DAHY2R2P, compared to that over HY2R2P, was attributable to relatively large amount of strong acid sites.

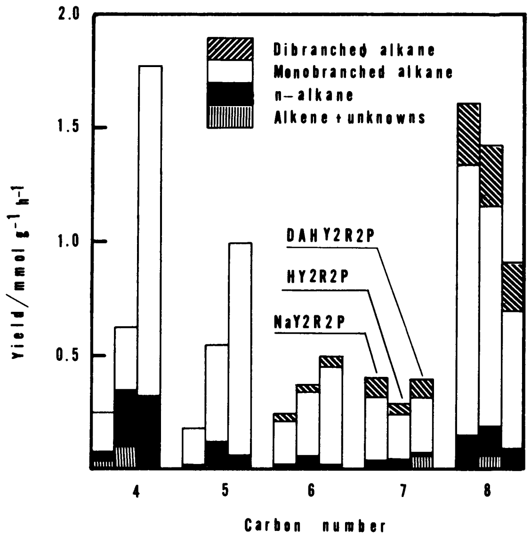

Fig. 3. Isomer distribution of product over NaY2R2P, HY2R2P, and DAHY2R2P. Reaction conditions: 240 °C, 1.5 MPa, $H_2/CO=3/2$, W/F=12.5 g-cat. h mol^{-1}, 1-octene feed rate=1.9 mmol g-cat.$^{-1}$ h^{-1}, after 2—3 h on stream.

Effect of H_2/CO Ratio. Effect of the partial pressure of H_2 and CO on products from DAHY2R2P was investigated by varying the H_2/CO ratio under the total pressure kept constant at 1.5 MPa. The obtained carbon number distribution is shown in Fig. 4. Isomer distribution is listed in Table 2. In the case of simple CO hydrogenation with high H_2/CO ratio large amount of methane was produced and the carbon number distribution shifted to light side. Activity decay was mitigated under these conditions, which was in agreement with the findings that the stabilized activity was obtained in case CH_4 was the main product.[8] Data obtained after 2—3 h on stream are shown in Table 2 and Fig. 4. Interestingly, only dimethyl isomers were detected for C_6 and C_7. Under these conditions the probability of skeletal isomerization could be high; the long chain alkenes and alkanes were virtually absent, resulting in the decrease in the rate of competitive adsorption and hydride transfer and hence prolonged lifetime of carbenium ion on acid site.[10,19]

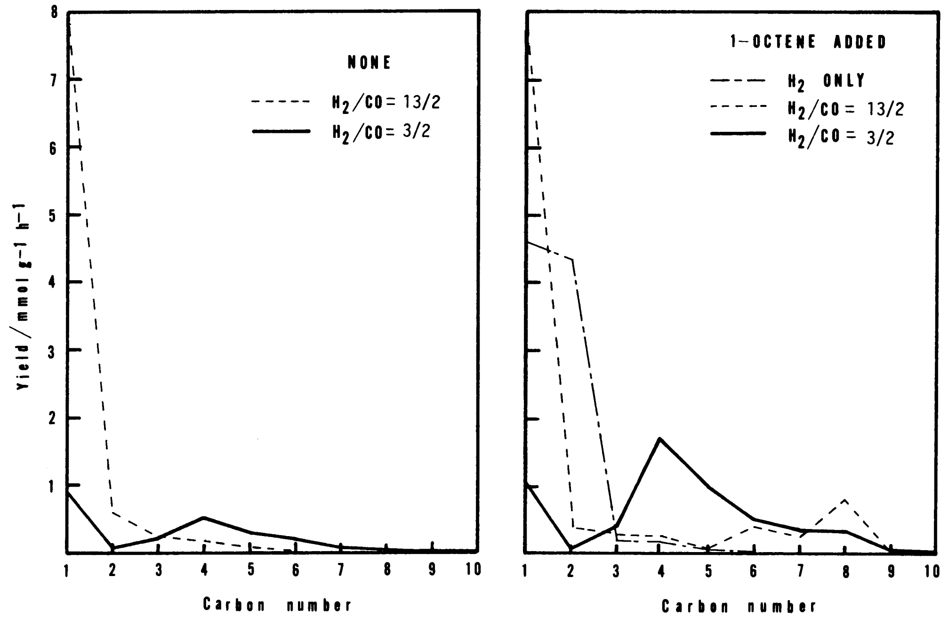

Fig. 4. Effect of H_2/CO ratio on carbon number distribution. Catalyst: DAHY2R2P; Reaction conditions: 240 °C, 1.5 MPa, W/F=12.5 g-cat. h mol^{-1}, 1-octene feed rate= 1.9 mmol g-cat.$^{-1}$ h^{-1}, after 2—3 h on stream.

Table 2. Effect of H_2/CO Ratio on Product Distribution[a)]

Reactant		H_2/CO only		1-Octene addition[b)]		
H_2/CO ratio		13/2	3/2	H_2 only	13/2	3/2
Carbon number	Product	Selectivity/%				
C_4	Butane	4.8	20.6	0.6	54.7	17.8
	Isobutane	94.0	78.9	95.1	45.2	81.3
	1-Butene	0.0	0.1	—	0.0	0.2
	t-2-Butene	1.2	0.3	4.3	0.1	0.5
	c-2-Butene	0.0	0.2	—	0.0	0.2
C_5	Pentane	1.4	6.3	—	41.2	6.0
	Isopentane	98.6	93.7	—	58.8	94.0
	Neopentane	0.0	0.0	—	0.0	0.0
	Alkenes + Unknown	0.0	0.0	—	0.0	0.0
C_6	Hexane	0.0	8.1	—	40.8	5.1
	2-M-pentane	0.0	51.5	—	35.4	56.9
	3-M-pentane	0.0	29.2	—	20.0	29.8
	2,2-DM-butane	17.7	0.0	—	0.2	0.0
	2,3-DM-butane	82.3	11.0	—	2.2	9.2
	Alkenes + Unknown	0.0	0.2	—	1.4	0.2
C_7	Heptane	0.0	8.4	—	17.4	3.3
	2-M-hexane	0.0	34.5	—	31.3	38.6
	3-M-hexane	0.0	31.3	—	33.7	31.5
	2,2-DM-pentane	0.0	0.0	—	1.6	0.0
	2,4-DM-pentane	100.0	8.4	—	6.2	9.5
	2,3-DM-pentane	0.0	10.7	—	5.1	9.5
	2,3,3-TM-butane	0.0	0.0	—	0.1	0.3
	Ethylpentane	0.0	6.3	—	2.5	2.8
	Alkenes + Unknown	0.0	1.3	—	2.1	4.5
C_8	Octane	—	8.0	—	12.2	8.0
	2-M-heptane	—	22.0	—	23.8	26.3
	3-M-heptane	—	26.1	—	27.3	32.8
	4-M-heptane (+ 3,4-DM-hexane)	—	8.2	—	8.5	9.8
	2,5-DM-hexane	—	7.8	—	8.6	7.3
	2,4-DM-hexane	—	10.4	—	9.6	9.5
	2,3-DM-hexane	—	5.2	—	3.1	4.9
	2,2-DM-hexane	—	0.0	—	1.6	0.0
	Alkenes + Unknown	—	12.3	—	5.5	1.4

a) Catalyst : DAHY2R2P; reaction conditions : 240°C, 1.5 MPa, W/F = 12.5 g-cat. h mol^{-1}, data obtained after 2—3 h on stream, M : methyl, DM : dimethyl, TM : trimethyl, *c* : cis, *t* : trans. b) 1-Octene feed rate : 1.9 mmol g-cat.$^{-1}$$h^{-1}$.

Contribution of acid-catalyzed cracking to the carbon number distribution in the case of 1-octene addition seems to be less significant with H_2/CO= 13/2 than with H_2/CO=3/2. The addition of 1-octene to syngas with H_2/CO=13/2 resulted in the slight increase in the yield of C_6 and C_7, as shown in Fig. 4. In both cases, methane production was virtually unchanged on addition of 1-octene, suggesting methane formed mostly derived from CO hydrogenation directly. The higher H_2/CO ratio gave lower cracking conversion of 1-octene and larger portion of straight-chain products (Table 2). This would be caused by facile metal-promoted hydrogenation of 1-octene and other alkenes desorbed before hydrocracking since alkanes are less susceptible to hydrocracking than alkenes.[1)] One must also consider the desorption of alkanes from carbenium ions promoted by higher concentration of activated hydrogen,[12,13,19)] resulting in decrease in the chance of skeletal isomerization.

In the absence of CO, 1-octene converted to methane and ethane owing to hydrogenolysis on Ru–Pt bimetallic alloy (Fig. 4). It should be noteworthy that isobutane comprises most of the C_4 fraction. It was imagined that a large portion of 1-octene underwent carbenium ion type reactions on acid sites and the formed primary products were further hydrocracked to methane and ethane on metallic site. The relatively high yield of ethane can be accounted for by the increasing order of activation energy of C–C bond breaking: $C_4 < C_3 \ll C_2$.[20] Small amount of CO (13%, $H_2/CO=13/2$) was sufficient to retard the hydrogenolysis of 1-octene. Further increase in CO fraction ($H_2/CO=3/2$) suppressed the methane formation during the courses of F–T synthesis. These findings imply negligible contribution of hydrogenolysis on metals to carbon number distribution of products in simple CO hydrogenation under standard conditions.

Effect of Contact Time. Effect of time factor on product distribution for DAHY2R2P was studied. The ratio of 2-M (2-methyl) and 3-M (3-methyl) isomers was employed as a measure of approach to equilibrium of the reaction products.[21,22] For simple CO hydrogenation, the short contact time (W/F=6.3 g-cat. h mol^{-1}) resulted in the 2-M/3-M ratios far below the equilibrium, as shown In Fig. 5. Low rate of 2-M isomers formation as primary products can be accounted for by a branching mechanism via protonated cyclopropanes.[22] With increasing contact time, the 2-M/3-M ratios increased.

The addition of 1-undecene resulted in the increase in 2-M/3-M ratios in C_6—C_8. This should come from the increased yield of 2-M isomers by cracking of 1-undecene and is in agreement with expectation based on carbenium ion-cracking mechanism.[23] These results suggest that there was only a minor contribution of cracking of heavy products to formation of C_6—C_8 fraction in the initial stage of CO–H_2 reaction. In the advanced stage, however, cracking of heavy fractions, which had been formed by oligomerization of light alkenes, seemingly occurred to a considerable extent.[1]

Effect of Temperature. Effect of temperature on the catalytic performance of DAHY2R2P is listed in Table 3. Simple CO hydrogenation at 300 °C exhibited remarkable increase in CO conversion and formation of methane and light hydrocarbons, compared to that at 240 °C. However, no significant change was observed for the *i/n* ratios of C_6—C_8 fractions. Slight decrease in the *i/n* ratios of C_4 and C_5 could result from contribution of cracking not preceded by formation of multibranched isomers. The addition of 1-undecene exhibited trends similar to simple CO hydrogenation. The yield of C_2 and C_3 was virtually unchanged on addition of 1-undecene at 300 °C, indicating little contribution of metal-promoted hydrogenolysis.

High temperature would lead to the promotion of CO hydrogenation on Ru-Pt alloy to produce light hydrocarbons. Simultaneously acid-catalyzed reaction should be also facilitated to give C_6—C_8 products rich in isoalkanes, although C_6—C_8 selectivity was significantly lowered. Thus the *i/n* ratios were kept at rather high levels while carbon number distribution

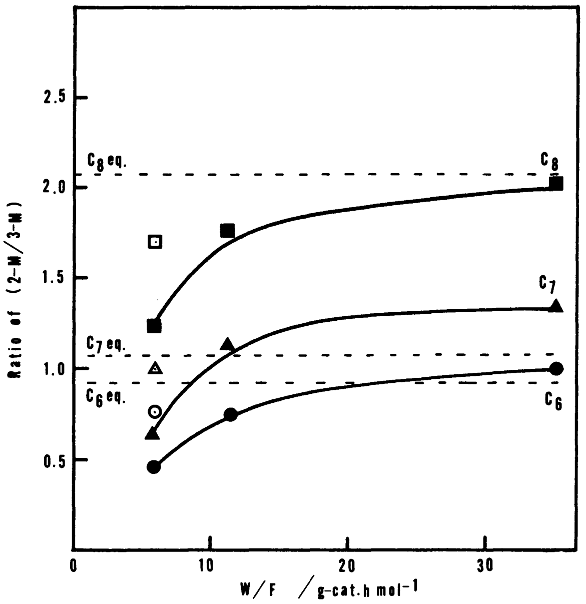

Fig. 5. Effect of time factor on 2-M/3-M ratio. Catalyst: DAHY2R2P; reaction conditions: 240 °C, 1.5 MPa, $H_2/CO=3/2$, 1-undecene feed rate=1.9 mmol g-cat.$^{-1}$h^{-1}, after 2—3 h on stream. 2-M/3-M ratio of products from simple CO hydrogenation: ●, C_6; ▲, C_7; ■, C_8. 2-M/3-M ratio of products from 1-undecene addition: ○, C_6; △, C_7; □, C_8. ⋯, 2-M/3-M ratio of thermodynamic equilibrium at 240 °C.

Table 3. Effect of Temperature on 1-Undecene Addition[a)]

Additive	None		1-Undecene	
Temperature/°C	240	300	240	300
CO conv./%	15.5	42.2	12.9	52.8
Carbon number	Distribution/mmol g-cat^{-1}h^{-1}			
C_1	0.40	7.01	0.79	6.39
C_2	0.04	0.69	0.04	0.76
C_3	0.10	0.48	0.27	0.90
C_4	0.23	0.39	1.24	1.34
C_5	0.17	0.31	0.96	1.12
C_6	0.11	0.12	0.89	0.81
C_7	0.06	0.04	0.53	0.53
C_8	0.03	0.02	0.08	0.12
C_9	0.01	0.02	0.01	0.03
C_{10}	0.01	0.00	0.00	0.02
C_{11}	0.00	0.00	0.00	0.01
C_{12^+}	0.00	0.00	0.00	0.00
	i/n ratio			
C_4	3.8	1.3	5.9	1.6
C_5	14.0	9.0	19.4	10.9
C_6	11.3	11.2	3.2	17.3
C_7	10.0	13.2	15.6	26.6
C_8	8.2	9.2	7.9	21.9

a) Catalyst : DAHY2R2P; reaction conditions : 1.5 MPa, W/F=12.5 g-cat. h mol^{-1}, $H_2/CO=3/2$, 1-undecene feed rate=1.9 mmol g-cat.$^{-1}$h^{-1}. Data obtained after 2—3 h on stream.

was largely changed. The deactivation degree of the catalysts was strongly dependent on the operating temperature. High temperature seemed to be favorable to durability of cracking activity. In this respect, suppression of light alkane formation at high temperature on metallic site should be indispensable to develop a gasoline-forming catalyst with good activity, selectivity and life for practical use.

Conclusion

Addition of 1-alkenes has been successful to elucidate the role of acid site and metallic site in CO hydrogenation over RuPtHY and RuPtDAHY zeolite catalysts. Carbon number distribution and products composition are dependent on factors such as the activity for hydrogenation of CO and alkene as primary products on the metals, the amount of acid sites, and the acid strength distribution on the support as well as operating conditions such as partial pressure of H_2 and CO, H_2/CO ratio, temperature, and time factor.

Acid sites are crucial to producing isoalkanes in gasoline range products via secondary reactions. There is a dependence of major reaction path on acid strength; while simple β-cracking of carbenium ion is favorable on strong acid sites, disproportionation of carbenium ion is feasible on relatively weak ones, effecting changes in carbon number distribution of the products from CO–H_2.

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