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ZEOLITE SUPPORTED Ru-Pt CATALYSTS FOR SELECTIVE FISCHER-TROPSCH SYNTHESIS

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Ruthenium-platinum bimetallic catalysts, prepared by simultaneous ion-exchange on zeolite HY, selectively produced from synthesis gas branched-chain paraffins in the C_4-C_{10} range, Exception to this was found for a catalyst with 4% Ru and 2% Pt by weight, which was highly active in exclusive formation of CH_4.

Product selectivity is the central problem in Fischer-Tropsch (F-T) synthesis, which usually gives products in C_1-C_{30} range, rich in straight-chain hydrocarbons. Limitations on hydrocarbon chain growth have recently been observed with the synthesis over ruthenium$^{1)}$ and iron$^{2)}$ encaged in zeolite Y. Improved selectivity for gasoline production has been observed with ruthenium$^{3)}$ or iron$^{4-6)}$/ZSM-5 composite catalysts. Formation of branched-chain hydrocarbons over ruthenium on silica-alumina or zeolite has been briefly reported.$^{7)}$ The so-called "isosynthesis" is known, in which sparingly reducible oxides give mainly C_4-C_8 branched-chain paraffins from synthesis gas, but the reaction conditions are very severe (400-500 $^{\circ}$C, 100-1000 atm).$^{8)}$

Isomerization of light paraffins using platinum-containing bifunctional catalysts has been practiced extensively in the petroleum refining industry.$^{9)}$ Objectives are either the manufacture of isobutane or the enhancement of octane rating of gasoline fraction. It occurred to us that Pt-Ru bimetallic catalysts encapsulated within the zeolite cages should be very efficient in forming F-T products rich in branched-chain hydrocarbons in the gasoline fraction. In order to verify this, a series of Y-zeolites containing either Ru or Ru and Pt was prepared. For example, a RuPtHY zeolite with 2% Ru and 2% Pt by weight on HY (designated H2R2P) was prepared by simultaneous ion exchange with an aqueous solution of $Ru(NH_3)_6Cl_3$ and $Pt(NH_3)_4Cl_2$. The samples of catalyst were dehydrated in situ and reduced with hydrogen at 673 K for 14 h. The synthesis reaction was carried out at 15 atm in a flow reactor at 513 K using a H_2:CO molar ratio of 1.5. The W/F was kept constant at 7 g h mol^{-1} (W = weight of the catalyst, F = molar flow of CO and H_2) unless otherwise noted.

The CO conversion and product selectivities over the Na2R (2%Ru by weight on NaY zeolite), Na2R2P, and H2R2P catalysts are given in Table 1. Data were obtained after 5 h on stream. The addition of Pt to Ru on NaY resulted in an increase in CO conversion and C_5^+ selectivity with a concomitant decrease in selectivity for CH_4 and olefins. With the H2R2P catalyst, the conversion was higher than with Na2R2P, and a pronounced selectivity for C_5^+ hydrocarbons is obtained. As is to be expected from high acidity of the HY zeolite, the H2R2P catalyst gave products rich in branched-chain hydrocarbons. For these three catalysts, the yield of C_{12}^+ was negligible.

Table 1. Activity and selectivity of supported ruthenium catalysts

Catalyst	CO conversion / %	Selectivity / wt% Carbon number CH_4	 C_4	 C_5^+	 branched/straight $i-C_4/n-C_4$	 olefin/paraffin C_2	 C_3	 C_4
Na2R	3.9	21	17	53	3.1	0.50	0.86	0.32
Na2R2P	7.7	6.9	16	72	4.7	0.25	0.45	0
H2R2P	11	7.2	22	66	7.9	0.14	0	0

The effect of Ru content on carbon number distribution and conversion, branched-chain/straight-chain ratios of paraffins, and C_4 and C_5^+ selectivity are shown in Fig. 1 and Table 2, respectively. Platinum content was constant at 2 wt%. As can be seen, the conversion and selectivity to heavier hydrocarbons increased with increasing Ru, except for H4R2P, which exhibited anomalously high activity with more than 90% selectivity for CH_4. Except fot H8R2P, $<$ 0.3% of the products was in the C_{11}^+ range. The branched/straight ratio for C_6-C_{10} given in Table 2 was determined on the assumption that all the products are paraffins. Such an assumption would be valid in the case of the catalysts containing Pt except H4R2P and H8R2P. In the case of H4R2P and H8R2P, over which olefins were formed to a considerable extent, the ratio may be overestimated. Obviously H2R2P gave the best result, the highest selectivity for C_5^+ branched-chain paraffins being obtained. Compared with the C_4 distribution, isopentane/n-pentane ratios are consistently much higher. The ratio decreased with increasing the carbon number from 5 to 10, the ratio for C_6-C_{10} being considerable lower than that for C_5.

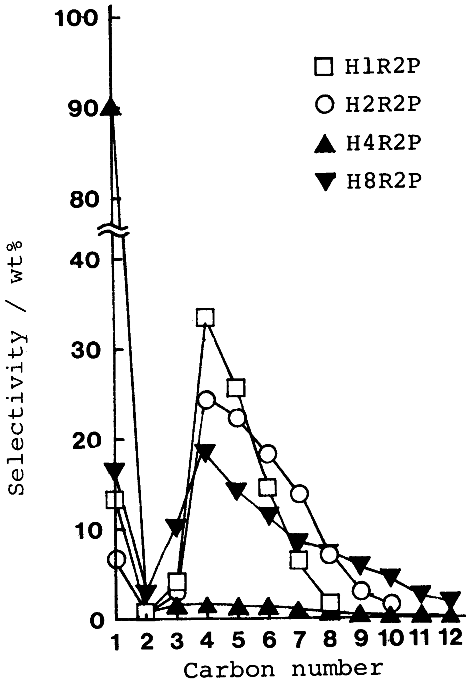

Fig. 1. Effect of Ru content on carbon number distribution.

Table 2 also shows the effect of space velocity (W/F) on the branched/straight ratios of C_4-C_{10} hydrocarbons produced over H2R2P. The ratio was markedly dependent on space velocity, with lower flows more normal paraffins being produced. The ratio obtained at W/F = 7 g h mol^{-1} is far above that predicted by thermodynamics. As the contact time increased, the ratio approached the thermodynamic value. This finding indicates that the branched-chain/straight-chain hydrocarbon production is controlled by kinetic factors and that the hydroisomerization of initially prevailing branched-chain olefins or paraffins to normal paraffins proceeds as the contact time

Table 2. Effect of ruthenium content, space velocity, and mechanical mixing

Catalyst	W/F /g h mol^{-1}	CO conversion / %	Selectivity / wt%							
			Carbon number		branched/straight			olefin/paraffin		
			C_4	C_5^+	C_4	C_5	C_6-C_{10}	C_2	C_3	C_4
H0.5R2P	7	1.5	17	33	7.5	15	5.0	0	0	0
H1R2P	7	3.6	31	31	9.3	28	6.5	0	0	0
H2R2P	7	11	22	66	7.9	40	16	0.14	0	0
H4R2P	7	85	1.6	5.2	0.21	4.4	3.0	0.02	1.02	1.48
H8R2P	7	19	16	56	0.32	1.7	1.0	0.16	1.70	1.02
H2R2P	17	28	13	79	4.1	24	12	0.06	0	0
H2R2P	33	38	16	62	1.4	3.5	3.3	0.03	0	0
Thermodynamic equilibrium(513 K)					1.2	3.2				
H2R+H2P	14	6.1	31	56	7.3	31	13	0.33	0	0
H2R	7	6.5	24	66	6.8	30	11	0.99	0	0
H4R+H2P	14	14	25	66	5.1	28	13	0.35	0	0
H4R	7	15	18	59	0.87	2.5	3.2	0.29	0.89	0.29

increases. It is also noteworthy that a pronounced selectivity for C_5-C_{12} hydrocarbons (79%) was observed at W/F = 17 g h mol^{-1}.

In order to pursue the reason of high selectivity for C_4-C_{10} branched-chain paraffins of the H2R2P catalyst, the H2R + H2P catalyst, which consisted of H2R mechanically mixed will an equal amount of H2P, was tested and compared with that of H2R2P and H2R (Table 2). To make equal the amount of CO introduced per Ru in the three catalyst, W/F was raised to 14 in the case of H4R + H2P. There seems to be little difference in carbon number distribution among the three catalysts. While the H2R catalyst gave products rich in branched-chain paraffins, platinum further increased the ratio in either way of addition. It is noteworthy that CO conversion over H2R2P is significantly higher than that over the others. It is considered that an intimate interaction of Ru and Pt is required for the appearance and duration of

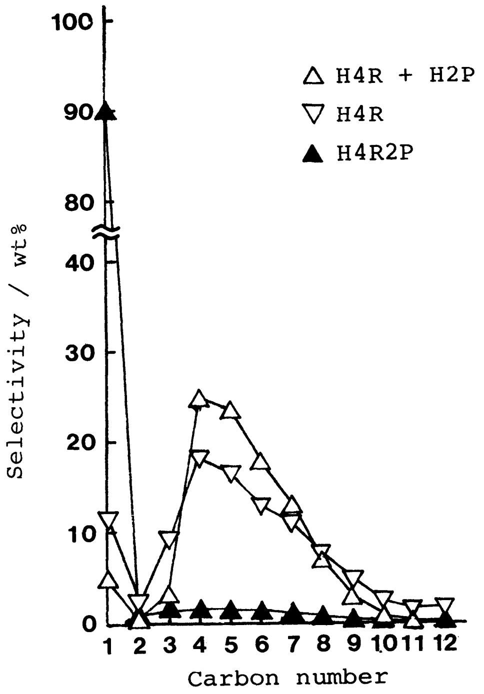

Fig. 2. Effect of mechanical mixing and simultaneous ion-exchange on carbon number distribution.

high activity. Platinum is an excellent hydrogenation catalyst and would be effective for hydrogenating the intermediate and/or preventing deactivation caused by carbide or coke formation. The H2P catalyst proved to be a very poor catalyst, CO conversion being less than 0.1%.

Similarly the activity of H4R + H2P (mechanical mixture of H4R + H2P) and H4R was compared with that of H4R2P. Figure 2 shows the carbon number distribution from the H4R + H2P, H4R2P, and H4R catalysts. In contrast to H4R2P, a pronounced selectivity for C_5^+ hydrocarbons was obtained with H4R + H2P. As shown in Table 2, over H4R + H2P, the formation of olefins was negligible except a small amount of ethylene and the products were as rich in branched-chain paraffins as those obtained from the H2R2P catalyst. On the other hand, the H4R catalyst produced a rather wide range of carbon number distribution, rich in olefins and low in the branched/-straight ratios. Supposedly the selectivity for branched-chain paraffins over H4R + H2P is obtained through secondary conversion over H2P of primary straight-chain hydrocarbons, especially olefins, produced over H4R. Thus the high methanation activity over H4R2P might be due to a formation of bimetallic clusters or alloy of Ru and Pt,10) effected during catalyst preparation. Surface measurements are in progress to clarify the nature of this interaction.

References

1) H.H. Nijs, P.A. Jacobs, and J.B. Uytterhoeven, J. Chem. Soc., Chem. Commun., 1979, 180, 1095; P.A. Jacobs, "Catalysis by Zeolites", ed by B. Imelik et al., Elsevier, Amsterdam (1980), p.293.
2) D. Ballivet-Tkatchenko, G. Coudurier, H. Mozzanega, and I. Tkatchenko, "Fundamental Research in Homogeneous Catalysis," ed by T. Ishii and M. Tsutsui, Plenum, New York (1979), Vol. 3, p.257.
3) W.O. Haag and T.J. Huang, U.S. Patent 4157338 (1978).
4) P.D. Caeser, J.A. Brennan, W.G. Garwood, and J. Ciric, J. Catal., 56, 274 (1979).
5) C.D. Chang, W.H. Lang, and A.J. Silvestri, J. Catal., 56, 268 (1979).
6) V.U.S. Rao and R.J. Gormley, Hydrocarbon Process, 59, 139 (1980).
7) D.L. King, J. Catal., 51, 386 (1978).
8) Y.T. Shah and A.J. Perrotta, Ind. Eng. Chem., Prod. Res. Dev., 15, 123 (1976).
9) See e.g., H.W. Kouwenhoven and W.C.van Zijil Langhout, Chem. Eng. Progr., 67, 65 (1971).
10) H. Miura and R.D. Gonzalez, J. Catal., 74, 216 (1982).

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