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Selective Synthesis of LPG from Synthesis Gas

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Synopsis. C_2–C_4 paraffins were produced from synthesis gas with selectivities higher than 80% at 300 °C and 21 atm by utilizing hybrid catalysts composed of a methanol-synthesis catalyst and a Y-type zeolite. The diffusion of lower olefins within zeolite pores and their hydrogenation on a methanol-synthesis catalyst were found to be important factors in controlling selectivity.

Liquified Petroleum Gas (LPG) is important for both home and transportation fuels. It is mainly composed of propane and butanes which maintain a proper vapor pressure at the ambient temperature. Several attempts have been made to produce LPG from synthesis gas with a precipitated Fe–Mn–Cu catalyst,[1] a fused-iron catalyst[2] and a supported molybdenum catalyst.[3] Since the above mentioned catalysts belong to the category of a Fischer -Tropsch catalyst, the hydrocarbon distribution follow the Anderson-Schluz-Flory distribution. This means that a significantly high selectivity regarding methane is inevitable.

Recently, Chang *et al.* have reported that the synthesis-gas conversions with H-ZSM-5 loading oxides of Cr, Zn, and Al give ethane with selectivities as high as 83% at around 400 °C and 100 atm.[4] The present authors showed that hydrocarbon mixtures with markedly different distributions were produced from synthsis gas using hybrid catalysts composed of a methanol-synthesis catalyst and zeolite.[5,6,7]

In the present paper, unique hybrid catalyst systems which give LPG with excellent selectivities are reported.

Experimental

The zeolite used as one component of the hybrid catalysts was prepared by treating a high-silica Y-type zeolite (supplied by Shokubai Kasei Inc., SiO_2/Al_2O=7.6) with steam at 450 °C for 1 hr(St-DAY). Methanol-synthesis catalysts, used as other components, were 4 wt% Pd/SiO_2,[6] home-made Cu–Zn–Al mixed oxide prepared following a method described by Shimomura *et al.*[8] (Cu:Zn:Al=40:23:37 in atomic ratio) or a commercially available Cu-based low-pressure methanol-synthesis catalyst (BASF S3-85). The Pd/SiO_2 catalyst was activated by treating with flowing hydrogen at 450 °C for 2 h. The copper-based catalysts were activated by flowing hydrogen at 300 °C for 3 h. The details of the preparative method regarding the hybrid catalysts has been described elsewhere.[5,6]

The reaction apparatus and procedures for a synthesis-gas reaction and a product analysis are the same as those described before.[6]

Results and Discussion

As demonstrated in Fig. 1, the methanol conversion on St-DAY and of synthesis-gas conversion with a hybrid catalyst composed of Cu–Zn(A) and St-DAY give hydrocarbon mixtures with extremely different compositions. The methanol conversion gives C_1–C_6 aliphatics containing significant amounts of olefins, aromatic hydrocarbons composed of mostly penta- and hexamethyl–benzenes (not shown in the figure), and coke. On the other hand, the synthesis-gas conversion gives C_2, C_3, C_4, and C_5 paraffins, exclusively, with a complete lack in aromatic hydrocarbons and a small amount of coke (0.6%).

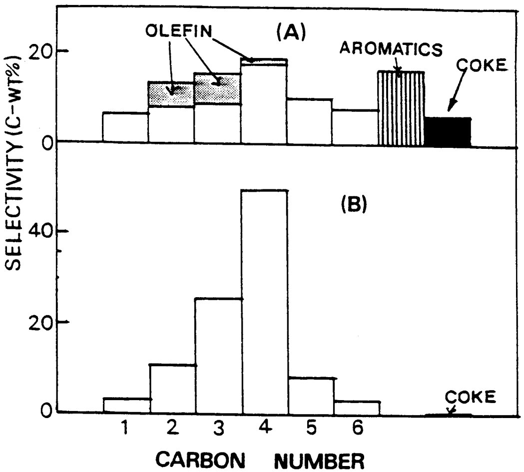

Fig. 1. Product distribution of (A) methanol conversion on St-DAY and (B) synthesis gas conversion on hybrid catalyst containing St-DAY.
(A): Methanol conversion on St-DAY only, 300 °C, 21 atm, 10% methanol in synthesis gas (H_2/CO=2/1), *W/F*=5g-cat h/mol, hydrocarbon yield= 97%, (B): Synthesis gas conversion on Cu-Zn(A)/St-DAY(1/1 weight ratio) 300 °C, 21 atm, H_2/CO=2/1, *W/F*= 10 g-cat h/mol, hydrocarbon yield=36.0%.

It has been known that methanol conversion with large-pore zeolite such as Y-type zeolite gives polymethylated benzenes as well as aliphatic hydrocarbons and coke because of its large pores. Thus, the new features of the products of synthesis-gas conversion with a hybrid catalyst, which are characterized by a lack of olefins, aromatics, and coke, should be attributed to some new catalytic effects caused by hybridization. This subject will be discussed later.

Table 1 shows the catalytic performances of 3 types of hybrid catalysts containing 3 different methanol-synthesis catalysts. It is apparent that all three catalysts give C_2–C_5 paraffins with selectivities higher than 90% and no aromatics while the hydrocarbon yield depends strongly on the catalyst. The distinction should be attributed to the activity of each methanol-synthesis catalyst since the first step of hydrocarbon formation in the present system is methanol formation. Although product patterns regarding the two hybrid catalysts containing Cu–Zn (A) and Cu–Zn (B) are quite similar, the pattern on the Pd/SiO_2 -based catalyst differs significantly from those on the former two catalysts. The latter one gives a product which is more rich in ethane and propane and is poorer in butanes. As discussed in more detail later, the most important reaction for controlling the product selectivity is the hydrogenation of the lower olefins which are inter-

Table 1. Hydrogenation of carbon monoxide with hybrid catalysts

Catalyst	Pd/SiO St-DAY^{2}	Cu-Zn (A) St-DAY	Cu-Zn (B) St-DAY	Cu-Zn (A) St-DAY	Cu-Zn (A) St-DAY
Temperature (°C)	300	300	300	270	320
W/F (g-cat h/mol)	10.1	2.7	3.4	3.2	3.2
Product Yield (%/CO fed)					
Hydrocarbon	6.4	15.0	35.7	5.1	20.0
Methanol	tr.	0.3	1.0	0.1	0.4
Dimethyl ether	tr.	1.0	4.3	1.6	0.9
Carbon dioxide	2.0	3.7	30.7	6.0	18.5
(Methanol[a])	(4.6)	(4.2)	(4.6)	(3.0)	(2.4)
Hydrocarbon distribution (carbon wt%)					
C_1	1.1	1.6	2.2	2.0	4.9
C_2	19.7	8.7	10.7	9.2	10.4
C_3	28.8	16.1	24.7	14.5	22.6
C_4	33.8	50.3	49.6	45.3	43.9
C_5	13.2	14.2	8.2	15.5	11.4
C_6^+	3.5	9.1	2.6	13.6	6.8
Pressure: 20 kg/cm^2, $H_2/CO=2/1$					

a) With methanol-synthesis catalyst only.

mediates from methanol to aromatics. Thus, it is assumed that the hydrogenation of the lower olefins, which terminates the carbon-chain growth, is more prominent for a Pd/SiO_2 based catalyst.

It should also be noted that the hydrocarbon yield in a synthesis-gas conversion with the hybrid catalyst exceeds the yield of methanol from synthesis gas with the methanol-synthesis catalyst alone under the same reaction condition. This fact could be interpreted to mean that while methanol fromation is controlled by thermodynamic equilibrium under the conditions adopted here, a quick conversion of methanol to hydrocarbon in situ by zeolite lowers the concentration, which enables a further conversion of synthesis gas beyond the thermodynamic limit of methanol formation. A clear tendancy of the product pattern to sift to the lighter side with increasing temperature is recognized, and is identical to that of methanol conversion on zeolites.

The drastic change in the product patterns from the methanol conversion system to the synthesis-gas conversion system should be attributed to some new reactions generated by the hybridization of the zeolite with the methanol catalyst. The change is most likely interpreted by the following scheme. As pointed out already,[6] the hydrogenation of lower olefins and the methylation by methanol of aromatic hydrocarbons are new and important reactions which control the product pattern of a hybrid catalyst system, as demonstrated in Fig. 2. The methanol produced on the methanol-synthesis catalyst moves to the zeolite surface to be converted to dimethyl ether and then to lower olefins.[9] Either dimethyl ether or olefins diffuse in the zeolite pores and some of them come out of the pores to the bulk gas phase. Olefins in the bulk-gas phase have a chance to be hydrogenated to lower paraffins, which terminate the carbon chain growth since methanol synthesis catalysts are active for olefin hydrogenation. When the zeolites with middle-size pores are used, aromatic hydrocarbons and coke are formed since olefins stay in the pores long enough to polymerize into aromatics due to their slow diffusion.[4,7] In the case where a large-pore zeolite (such as a Y-type zeolite) is used, almost all of lower olefins come out of the pores, without polymirizing into aromatics, and are hydrogenated to paraffins on the methanol synthesis catalyst because of the three-times higher diffusion rate in the zeolite pores than that for a middle-pore zeolite (mordenite).[10]

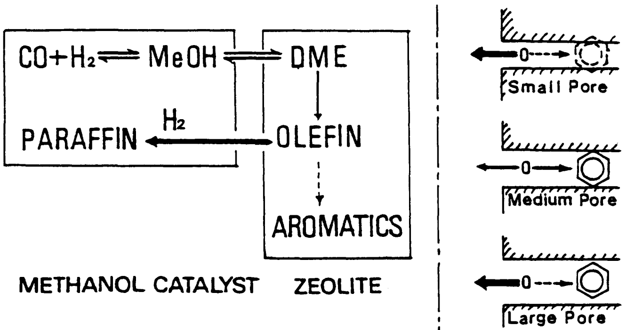

Fig. 2. Reaction path for hydrocarbon formation from synthesis gas on hybrid catalyst containing methanol synthesis catalyst and zeolite.

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