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SELECTIVE SYNTHESIS OF AROMATIC HYDROCARBONS FROM SYNTHESIS GAS

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Aromatic hydrocarbons, whose major components were penta- and hexa- methyl benzenes, were produced with the selectivity of 27% from synthesis gas at 350 °C and under 21 atm with hybrid catalysts containing Pd/SiO_2 catalyst and high silica mordenites. Steam treatment of the high silica mordenite, which cause the hydration, promoted the selectivity of aromatic hydrocarbons and suppressed dramatically the coke producing ability of the hybrid catalyst upon synthesis gas conversion.

It has been reported that light paraffins or aromatic hydrocarbons were directly produced from synthesis gas on hybrid catalysts composed of methanol synthesis catalyst such as Zr or Zn-Cr mixed oxide and H-ZSM-5 under severe conditions (83 atm and 427 °C).1) The reaction system is characterized by the facts that synthesis gas conversion is not restricted by the thermodynamical equilibrium of methanol formation from synthesis gas2) and that the product are rich in aromatics, which could not be expected for the traditional Fischer-Tropsch synthesis.3)

The authors have shown that synthesis gas reaction over the hybrid catalysts composed of Pd/SiO_2 (methanol synthesis catalyst) and H-ZSM-5 give aromatic hydrocarbons with selectivities between 10% and 30% under moderate conditions such as 350 °C and 21 atm.4) In the present work it has been found that a steam treated high silica mordenite (St-DAM) gave aromatic hydrocarbons with high selectivity when it was subjected to the synthesis gas reaction in combination with Pd/SiO_2.

A Pd/SiO_2 catalyst was prepared following the method described in elsewhere.4) The silica gel used as carrier was a commercially available one (Fuji Davison ID, specific surface area: 270 m^2; pore volume: 1.1 cm^3/g; mean pore diameter: 140 Å). Palladium loading was 4% by weight and its dispersion was 14% (by CO chemisorption). The catalyst was activated by reducing in flowing hydrogen at 400 °C for 4 h. H-mordenite was a commercially available mordenite (Norton Zeolon-100H). High silica mordenite (DAM) were prepared by treating Zeolon-100H with 8 mol/dm^3 hydrochloric acid solution at 100 °C for 24 h to extract aluminium.5) After extraction it was dried in an air oven at 120 °C for 24 h and then calcined at 450 °C for 3 h. St-DAM was prepared by passing steam through the bed of DAM at 450 °C at the rate of 1 g of steam per gram of zeolite per hour followed by calcining in flowing nitrogen at 450 °C for 30 min. The preparative procedure of the hybrid catalysts and the method of synthesis gas conversion are similar to those described

Table 1. Physical Properties of Zeolite

Zeolite	Acid amount (meq./g)	Al content (mmol/g)	SiO_2/Al_2O_3 (mole Ratio)	Crystallinity[a)] (at D = 3.96 Å)
H-M	3.74	2.02	14.6	100
DAM	1.24	0.61	53.0	99
St-DAM	0.96	0.60	54.1	107

a) Relative value, H-M = 100, Determined by peak height.

before.[4)] Acid amount was determined by the amount of chemisorbed NH_3 at room temperature. Infrared spectra of adsorbed pyridine were recorded on Jasco A-3 spectrophotometer following the method described by Take et al.[6)]

Physical properties of zeolites such as SiO_2/Al_2O_3 ratio, acid amount, content of aluminium, and crystallinity of zeolite are shown in Table 1. It is clear that acid treatment causes a marked increase in SiO_2/Al_2O_3 ratio attributed to the extraction of aluminium and steam treatment causes slight increase in its level. In spite of the drastic change in the chemical composition the crystallographic structure of mordenite were substantially unchanged during acid treatment or steam treatment. It is also apparent from Table 1 that acid amounts of mordenites were 1.5-2 times as much as aluminium contents of mordenites. That is, acid amounts of H-M and DAM are twice as much as aluminium content whereas the acid amount of steamed mordenite (St-DAM) is 1.5 times as much as the content of aluminium in the zeolite. Since as it will be shown later DAM is largely hydrated by steam treatment the change in the stoichiometry of ammonia adsorption would be attributed to the poisoning of some acid site by adsorbed water.

Figure 1 shows infrared spectra of adsorbed pyridine on H-M, DAM and St-DAM. Four eminent adsorption bands were observed, which could be attributed to (1) the mixture of adsorbed pyridine coodinatively bonded to Lewis acid sites plus adsorbed pyridine with hydrogen bonding (1450 cm^{-1}), (2) the mixture of adsorbed pyridine on Brösted and Lewis acid sites (1490 cm^{-1}), (3) pyridinium ion formed on Brönsted acid sites (1540 cm^{-1}) and (4) hydrogen bonded

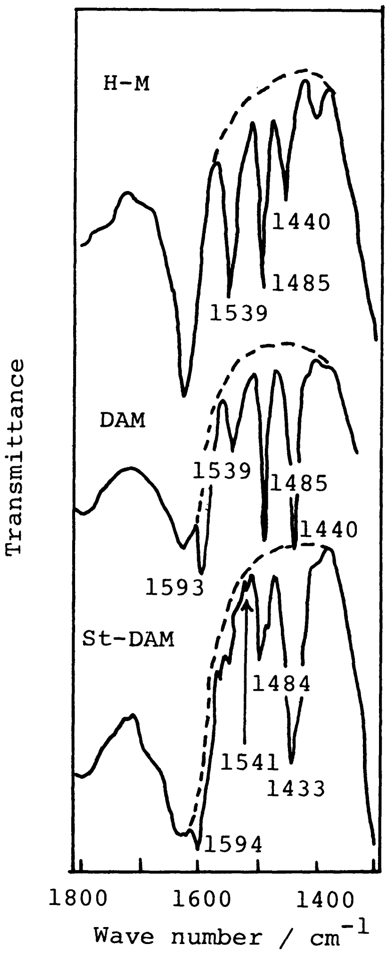

Fig.1. IR spectra of adsorbed pyridine, adsorbed and evacuated at 150 °C.

Table 2. Performances of Synthesis Gas Conversion [a]

Catalyst	Pd/SiO_2+H-M[b]	Pd/SiO_2+DAM	Pd/SiO_2+St-DAM
Product yield (%/CO Feed)			
Hydrocarbon	8.0	9.7	10.6
Carbon dioxide	3.3	7.2	6.5
Coke[c]	3.1	2.0	0.4
Hydrocarbon distribution (carbon wt%)			
Aliphatics			
C_1	12.6	6.0	2.8
C_2	39.9	22.9	16.6
C_3	24.8	28.3	30.0
C_4	5.3	16.6	17.4
C_5	2.2	4.9	4.8
C_6	2.2	2.2	1.5
C_7+	2.0	0.1	-
Aromatics [d]			
A_6	0.2	-	-
A_7	0.1	-	-
A_8	0.7	-	0.1
A_9	0.7	0.1	0.6
A_{10}	1.2	1.8	8.9
A_{11}	5.1	15.2	16.2
A_{12}	2.6	1.8	1.0
A_{13}+	0.1	-	-
Total aromatics	10.7	18.9	26.8

a) 21 atm, 350 °C, $H_2/CO = 2/1$, W/F = 10 g·h/mol.

b) Mixing ratio 1/1 by weight.

c) Determined by clemental analysis of used catalyst.

d) A_{10}^{+} contains small amount of naphthalene derivatives.

pyridine (1590 cm^{-1}).[6] It is obvious that acid treatment of mordenite causes the decrease in Brönsted acid site and partial hydration and that additional steaming has caused a drastical decrease in Lewis acid site and a marked increase in hydrated acid site.

Data on the results of synthesis gas conversion over the hybrid catalysts which are expressed as the average values of about four hours run (Table 2), indicate that the yields of hydrocarbons containing coke are about 11%, irrespective of mordenite species.

It should be noted that methane selectivity is lower for DAM based catalyst, especially that on St-DAM based catalyst is quite low. By contrast, the selectivity of C_3 and C_4 paraffins is higher for DAM or St-DAM based catalyst than for H-M based catalyst which suggest the polymerization ability of mordenite for methanol is promoted by extracting aluminium. Another characteristic features which should be noted are that the selectivity of aromatic hydrocarbons is noticeably enhanced while the production of coke is drastically suppressed by the steam treatment of high silica mordenite. As it has been accepted generally, the reaction path of methanol conversion on zeolite is supposed to be composed following of unit reactions: (1) dimethyl ether formation (2) dimethyl ether to olefins, (3) olefins to aromatics (4) probably aromatics to coke and (5) transfer hydrogenation of olefins or alkyl carbonium ion by hydrogen which generate during aromatics or coke formation.

According to the beforementioned reaction path, steaming of DAM is thought to be quite effective in suppressing the rate of reaction (4). By suppressing coke formation aromatic hydrocarbons can be recovered as product. The higher molecular weight of product paraffins on St-DAM can be explained by the reduced coke formation. Because the transfer hydrogenation of lower olefins or alkyl carbonium ion by hydrogen generated during coke formation, which is effective in terminating carbon chain growth, is naturally suppressed.

Although the reason why coke forming activity of mordenite is suppressed by extracting aluminium and especially by steaming it is not clear yet. It is supposed that the drastical decrease in acid amount, which mean the decrease in the acid density and the change in some unidentified acid character, which would be caused by the hydration of acid sites might correlate closely to the decrease in the activity.

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