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Direct Production of Liquid Hydrocarbons from Ethane with Hybrid Catalysts

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Ethane could be converted effectively to liquid hydrocarbons over hybrid catalysts prepared by mixing a dehydrogenation catalyst of ethane with ZSM-5 type zeolites. However, no liquid hydrocarbons were produced from ethane on ZSM-5 alone.

Many researches on the production of liquid fuels from natural gas via oxidative coupling of methane have been reported.[1-2] In this process, ethane and ethylene which are the main products of oxidative coupling of methane should be converted to liquid hydrocarbons over ZSM-5 type zeolites. However, it is difficult to convert ethane to liquid hydrocarbons directly over the zeolites alone because of its low reactivity in the reaction, whereas ethylene is effectively converted to liquid hydrocarbons on the same zeolites. Therefore two consecutive reactions, the dehydrogenation of ethane to ethylene and the polymerization of ethylene to liquid hydrocarbons are necessitated. Ethane is usually dehydrogenated by pyrolysis with the heat evolved from oxidative coupling of methane.[2] Although ethane can be also catalytically dehydrogenated, a higher temperature, over 1073 K, is needed for higher conversion, because the dehydrogenation is thermodynamically unfavorable endothermic reaction.

In this letter, a combined catalyst system named hybrid catalyst, was developed to convert ethane directly to liquid hydrocarbons in a single catalyst bed at around 873 K. Hybrid catalysts were prepared by admixing catalysts for ethane dehydrogenation with ZSM-5 type zeolites. Using the catalysts, it is expected that ethane is first dehydrogenated to ethylene, which is polymerized *in situ* to form liquid hydrocarbons with ZSM-5.

A dehydrogenation catalyst was prepared by impregnating a commercially available alumina(JRC-ALO-4, surface area=200 m^2/g) with platinum chloride, from its aqueous solution, drying in an air oven at 673 K for 15 h, heating slowly to 823 K and calcining for 2 h at this temperature. Platinum loading was 5 wt% as metal. ZSM-5 type zeolites(SiO_2/Al_2O_3 mole ratio=50) were synthesized according to the method described in a patent.[3] The zeolites were ion-exchanged with H^+ or Mg^{2+} in aqueous solutions of ammonium nitrate or magnesium nitrate.

Hybrid catalysts were prepared by physically mixing the dehydrogenation catalyst with the zeolites in the ratio of 1:4 by weight. They were activated in hydrogen flow at 673 K for 15 h. These catalysts were tested using a fixed-bed reactor with a conventional gas-flow system under atmospheric pressure.

Reaction products were analyzed by gas chromatography. The conversion of ethane and the selectivity of products were calculated on the basis of reacted ethane.

The results of ethane conversion are shown in Table 1. No liquid hydrocarbons were produced over the H-ZSM-5(H-50) alone, but CH_4 was produced. With the hybrid catalyst(Pt/Al_2O_3+H-50), on the other hand, considerable amounts of ethane were mainly converted to aromatic hydrocarbons which are designated A_6(benzene), A_7(toluene), A_8(xylenes), and A_{9+} in Table 1. The hybrid catalyst prepared from Pt/Al_2O_3 and Mg ion-exchanged zeolite(Mg-50) also gave almost the same result.

Table 1. Ethane to liquid hydrocarbons over ZSM-5 zeolites and hybrid catalysts
Temp=873 K, C_2H_6/N_2=1/4 mol/mol, Catalyst=1 g, W/F=10 g h/mol

Catalyst	Conv./%	Selectivity/%								
		C_1	C_2	C_3	C_4	C_{5+}	A_6	A_7	A_8	A_{9+}
H-50	0.5	96.0	0	4.0	0	0	0	0	0	0
Pt/Al_2O_3+H-50	20.1	20.4	0	5.1	0	0.5	32.6	23.8	3.5	14.1
Pt/Al_2O_3+Mg-50	19.8	17.4	0	7.9	0	0.6	41.4	20.4	2.7	10.0
Pt/Al_2O_3&Mg-50	12.5	13.1	0	29.6	0	0.5	35.8	13.6	1.1	6.2

The calculated conversion of ethane to ethylene at the equilibrium is about 15.7 % at 873 K, and at atmospheric pressure. The higher conversion was obtained with the hybrid catalysts as shown in Table 1. Whereas, if ethane was passed through the two catalyst beds composed of Pt/Al_2O_3 and Mg-50 in series, with Pt/Al_2O_3 being upper side, ethane conversion was 12.5 %, being less than the equilibrium conversion, as shown in Table 1. It is clear that the equilibrium limit of ethane to ethylene could be overcome in the presence of hybrid catalysts because ethylene produced by the dehydrogenation of ethane was immediately polymerized to liquid hydrocarbons.

References

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