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Selective Synthesis of Ethylene from Synthesis Gas over Hybrid Catalyst System

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Selective synthesis of ethylene from synthesis gas has been investigated by using a hybrid catalyst system which was composed of an ethanol synthesis catalyst and zeolite as a dehydration catalyst. Ethylene was produced with a 45% selectivity from synthesis gas by the combination of Rh-Ti-Fe-Ir/SiO_2 catalyst and H-Silicalite catalyst.

Many efforts have been made for the selective synthesis of lower olefins, such as ethylene and propylene, directly from synthesis gas by modified Fischer-Tropsch syntheses. However, difficulties are still present to overcome the restriction of Schulz-Flory distribution of produced hydrocarbons. On the other hand, it is well known such olefins are produced selectively from methanol over some zeolite catalysts as results of moderate acid properties and shape selective effects.1)

Several combination catalysts composed of a synthesis gas catalyst and zeolite have been applied for a control of product selectivity. For example, Fujimoto et al. showed a physically mixture of a methanol synthesis catalyst and Y-type zeolite for a selective synthesis of lower paraffins.2) We are interested in a selective synthesis of ethylene directly from synthesis gas. Recently, high performance catalysts for ethanol synthesis have been developed.3) From this point of view, we have studied a possibility of selective synthesis of ethylene from syngas by hybrid systems composed of a ethanol synthesis catalyst and a zeolite as a dehydration catalyst.

A multi promoted Rh/SiO_2 catalyst, Rh-Ti-Fe-Ir/SiO_2 for ethanol synthesis, was prepared by impregnation of a SiO_2(Davison grade 57) with an ethanol solution containing $RhCl_3 3H_2O$, $TiCl_4$, $FeCl_3 6H_2O$, and $IrCl_4 H_2O$. After impregnation, the catalyst was dried carefully by a rotary evaporator up to 120 °C, and then reduced gradually in a H_2 flow at the temperature from 20 °C to 400 °C, finally at 400 °C for 2 h.3) ZSM-5(SiO_2/Al_2O_3=47) and Silicalite(SiO_2/Al_2O_3=2100) were prepared according to Mobil and UCC patents, respectively.4) Commercially available zeolites such as Zeolon and γ-Al_2O_3(Harshow) were also used. Syngas reaction was carried out using a pessurized fix-bed flow type reactor。 Rh-Ti-Fe-Ir/SiO_2(Catalyst A) was charged on the top of zeolite(Catalyst B) without mixing each other in a same reactor tube. The effluent gas was kept at 180 °C and directly introduced to GC and analyzed. A synthesis gas (H_2/CO=1/1) which was fed contained 10 volume% of Argon gas as a standard.

Table 1 shows the result of syngas reaction over various combination catalysts. In every run, CO conversion was not affected by the presence of a dehydration catalyst(Catalyst B). Product selectivity was not changed in the case of SiO_2, that is, C_2-oxygenates such as ethanol and acetaldehyde were produced mainly. On the other hand, the selectivity was much influenced by the dehydration catalyst. For example, ethanol was converted to diethylether in place of ethylene in a case of γ-Al_2O_3 as a result of intermolecular-dehydration. H-Silicalite was proved to be a good catalyst for the selective conversion of ethanol to ethylene under the condition of syngas conversion. An effectiveness of ethanol conversion to ethylene goes up to 90%. Zeolon catalysts are also favorable for production of ethylene. In contrast, most of ethanol was converted to methane at the initial stage in a case of H-ZSM-5 and ethanol conversion was decreased quickly with time to give no effect on the selectivity. Mordenite, as well as H-ZSM-5, was not effective for ethanol conversion to ethylene. In conclusion, it has been found that ethylene is produced with a 45% selectivity by one-path from syngas conversion over a hybrid catalyst composed of an ethanol synthesis catalyst(Rh-Ti-Fe-Ir/SiO_2) and H-Silicalite. One of advantages of this system is that other olefins such as propylene and butene are produced negligibly compared with ethylene.

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Table 1. Synthesis gas conversion over hybrid catalyst system

		Product selectivity in carbon efficiency / %									
Catalyst B	CO conv.	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	MeOH	EtOH	EtOEt	C_2-oxy.	CO_2
SiO_2	6.3	21.5	0.1	1.3	0.4	0.5	3.7	50.7	0.0	65.0	4.2
γ-Al_2O_3	6.2	31.3	7.2	2.0	3.2	0.5	4.5	17.7	22.4	41.1	5.8
H-Silicalite	6.2	32.7	44.7	3.6	2.4	1.2	5.9	0.0	1.5	5.8	3.1
Zeolon-500H	6.1	34.2	41.9	11.9	0.0	1.6	0.0	0.0	0.0	0.0	10.3
Zeolon-200H	6.2	44.8	23.9	5.2	0.0	8.7	0.2	0.0	0.0	0.0	10.9
H-ZSM-5[a)]	6.2	66.0	1.8	4.6	2.2	1.1	6.5	1.4	0.0	5.1	11.5
H-ZSM-5	6.1	23.2	0.5	1.4	0.7	0.3	12.2	42.8	0.0	55.6	3.5
Mordenite	6.2	50.9	0.0	7.5	0.0	19.7	0.0	0.0	0.0	0.0	15.0

Catalyst A:Rh-Ti-Fe-Ir(1:1:0.3:0.5)/SiO_2,Rh content:4.7wt%, catalyst charge:0.5 g. Catalyst B:Dehydration catalyst, catalyst charge:1.5 g;Reaction conditions:260 °C, 50 kg/cm^2, 100 ml/min, H_2/CO=1/1; Data were obtained at a time on stream of 1 h. a): at a time on stream of 0.5 h.; C_2-oxy.: Sum of C_2H_5OH, CH_3CHO, CH_3COOH, and $C_2H_5OC_2H_5$; EtOH:C_2H_5OH, MeOH:CH_3OH, EtOEt:$C_2H_5OC_2H_5$.

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