Highly Selective Synthesis of Ethene from Methanol on a Novel Nickel–Silicoaluminophosphate Catalyst

Tomoyuki Inui,* Suphot Phatanasri, and Hirokazu Matsuda

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

A novel Ni–silicoaluminophosphate catalyst synthesized by rapid crystallization exhibited prominently high selective synthesis of ethene from methanol under total conversion conditions and temperatures around 450 °C.

The synthesis of light alkenes from methanol is important in C_1-chemistry. Although narrow pore zeolites such as chabazite[1] and ZSM-34[2] are effective for this purpose, the short life caused by the coke deposit is a serious obstacle with these catalysts. ZSM-5 catalyst does not suffer from heavy coke deposit owing to its three-dimensional pore structure.[3] However, typical ZSM-5 catalyst is not selective to the formation of light alkenes[4] owing to consecutive oligomerization and aromatization on its strong acid sites. Although some modification of ZSM-5 with base compounds such as P,[5] Mg,[6,7] Zn,[6] Ca,[6,7] Sr,[7] and B[6] to reduce the acid strength have been proven to enhance the selectivity towards light alkenes, the catalytic activity was greatly reduced. Recently, one of the family of silicoaluminophosphate(SAPO-*n*), SAPO-34, having the chabazite structure, was found to exhibit good catalytic performance for the conversion of methanol to light alkenes.[8] However, the distribution among C_2, C_3, and C_4 alkenes was roughly comparable.

For further improvement, we have synthesized a nickel-incorporated silicoaluminophosphate of the 34 type, designated as Ni–SAPO-34, with a Si : Ni atomic ratio of 40 by adopting our intrinsic rapid crystallization method.[9] The catalyst was prepared as follows: 18 ml of water, 71 ml of 20% aqueous tetraethylammonium hydroxide, 12 g of 30.1 wt% SiO_2 sol (Cataloid 30 of Shokubai Kasei Corp.), 0.44 g of $Ni(NO_3)_2 \cdot 6H_2O$ (guaranteed grade reagent), and 14 ml of 85% phosphoric acid were poured successively into 41 g of aluminium isopropoxide while vigorously stirring with an

Table 1. Effect of reaction temperature on product distribution of methanol conversion on Ni–SAPO-34 catalyst.

Reaction temp. /°C	Product distribution (C-wt %)											MeOH conv. /%
	C_1	C_2	$C_2{=}$	C_3	$C_3{=}$	C_4	$C_4{=}$	C_{5+}	DME[a]	CO	CO_2	
250	0.40	0.64	80.58	0.34	3.83	0.17	1.39	0.98	11.66	—	—	96.90
300	0.28	0.31	71.90	0.84	15.80	0.51	7.29	2.55	0.52	—	—	99.44
350	0.16	0.32	70.75	0.68	17.67	0.20	7.91	2.14	—	—	0.17	100
400	0.61	0.47	65.25	0.77	18.40	0.12	8.84	5.47	—	—	0.06	100
450	1.50	1.02	88.04	0.15	5.26	0.03	2.46	1.25	—	—	0.28	100
500	6.11	0.90	69.14	0.14	8.06	0.05	5.92	6.73	—	2.44	0.49	100
550	13.22	2.80	54.81	0.18	6.84	0.03	1.76	1.70	—	16.66	1.98	100
600	16.56	2.78	53.40	0.28	4.22	0.03	0.85	0.52	—	19.04	2.32	100

[a] DME = dimethyl ether.

Ultra-disperser. The gel mixture obtained was milled for an hour by a motor-driven mortar, Yamato-Nitto UT-21, and was charged in a pyrex glass tubular vessel of 5.8 cm inner diameter. It was put in a one-litre stainless steel autoclave. The atmosphere in the autoclave was replaced by N_2 with a 3 kg cm^{-2} gauge. This was heated from room temperature to 160 °C and then up to 200 °C with a constant heating rate of 1.5 °C min^{-1} and 12 °C h^{-1} respectively. The temperature was then kept at 200 °C for 4 h. The crystals produced were washed with distilled water by using the centrifugal separator, dried overnight at 100 °C, and then calcined in air at 600 °C for 3.5 h. The prepared crystallites were tableted and crushed to 7—15 mesh to provide the reaction.

The *X*-ray diffraction pattern was almost the same as that of SAPO-34 cited in the patent literature.[10] The Brunauer–Emmett–Teller (B.E.T.) surface area of this sample was 403 $m^2\ g^{-1}$. The acidity of catalyst measured by NH_3-temperature programmed desorption (TPD) was considerably weaker than that of SAPO-34.[5] The methanol to hydrocarbon conversion reaction was carried out using continuous flow apparatus under the following conditions: total pressure 1 atm; partial pressure of methanol 0.20 atm; balance gas N_2; weight of the catalyst used 0.20 g; GHSV 2000 h^{-1}; reaction temperature 250—600 °C. The reaction products were analysed by two flame-ionisation detector (FID) and two thermal conductivity detector (TCD) gas chromatographs. Columns used were VZ-10 for gaseous hydrocarbons, silicon OV-101 for gasoline range hydrocarbons, Porapack T for MeOH and MeOMe, and activated carbon for CO and CO_2.

The reaction temperature for methanol conversion was varied from 250 to 600 °C with each 1 h of time on stream. Fresh catalyst was used on each run. As shown in Table 1, the highest selectivity towards ethene (nearly 90%) was achieved at 450 °C. The catalyst performance was maintained at this temperature for 13 h. During this time there was no significant change in the methanol conversion or the ethene selectivity. The acidity of Ni–SAPO-34, which is weaker than that of SAPO-34 and just sufficient for dehydration of dimethyl ether, must be responsible for this unusual highly selective ethene synthesis.

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