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CONVERSION OF METHANOL INTO OLEFIN-RICH GASEOUS HYDROCARBONS OVER SUPPORTED ALUMINUM DIHYDROGENPHOSPHATE CATALYST

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Supported aluminum dihydrogenphosphate serves as an excellent catalyst for the decomposition of methanol to give olefin-rich gaseous hydrocarbons with depression of the formation of methane, carbon monoxide, and carbon dioxide.

The production of hydrocarbons from methanol is expected to become an important process for the manufacture of a clean fuel or fundamental raw materials such as ethylene and propylene from coal, because methanol can be selectively produced from synthesis gas obtained by coal gasification.[1)] However, no catalyst other than zeolites[2)], polyphosphoric acid[3)] or zinc iodide[4)] for the conversion of methanol into gaseous or gasoline-range hydrocarbon products has been reported until present time. In this communication, we wish to report the olefin-rich gaseous hydrocarbon synthesis from methanol over supported aluminum dihydrogenphosphate catalyst and the results of methanol conversion with some supported salts as catalysts.

The reaction was carried out under atmospheric pressure using a previously reported[5)] micro reactor fitted with a microfeeder and a vaporizer. Argon was employed both as diluent gas and internal standard gas for determination of the gaseous products by gas chromatographic analysis. Ice-trapped methanol and water were also analyzed by gas chromatography. Catalysts were prepared by impregnation of silica-alumina (Neo-bead DL-4 obtained from Mizusawa Kagaku Corp.) with HCl aq. soln. of $Al(H_2PO_4)_3$, $NiSO_4$, or $ZnCl_2$ and dried at 400°C for 1.5 hr in the stream of argon prior to use.

Results are listed in Table 1. With supported $NiSO_4$ or $ZnCl_2$ or a support alone as catalysts, methanol mainly decomposes to CO, CO_2, or CH_4, except selective formation of dimethyl ether in the case of supported $ZnCl_2$ at 300°C. However, decomposition of methanol catalyzed by supported $Al(H_2PO_4)_3$ produced olefin-rich $C_2{\sim}C_4$ hydrocarbons in 20~60 % yield (based on carbon fed) in much preference to CO, CO_2, or CH_4. Hydrogen (trace) and water were detected as non carboneous products. Dimethyl ether, we believe, is not an undesirable product but an intermediate or an equilibrium species with methanol from consideration of LHSV or temperature dependence of its yield. It is reported that $Al(H_2PO_4)_3$ decomposes at 180°C to give $Al_2O_3 \cdot 3P_2O_5$[6)], but it is probable in our case that $Al(H_2PO_4)_3$ had changed into another species such as $AlCl_3 \cdot 3H_3PO_4$ during the impregnation for the preparation of the catalyst. Further work to clarify the catalytically active species and the reaction course is now in progress.

Table 1 Yields of catalyzed decomposition products of methanol[a)]

Catalyst[b)]	$Al(H_2PO_4)_3$					$NiSO_4$	$ZnCl_2$		None[c)]
Temp.(°C)	425	400	400	400	375	375	400	300	400
LHSV	0.18	0.71	0.18	0.09	0.18	0.18	0.18	0.18	0.18
CH_3OH[d)]	4.4	22.3	8.5	3.2	8.2	17.0	tr	11.9	20.2
CH_3OCH_3	13.3	20.1	31.6	1.1	42.2	30.1	0.0	83.1	49.1
CO[e)]	8	4	1	1	1	15	34	0	13
CO_2	tr	tr	tr	tr	tr	3.3	32.7	0.4	0.5
CH_4	26.1	8.6	7.6	9.3	3.2	20.8	20.3	0.0	8.9
C_2H_6	3.1	0.4	1.1	3.1	0.9	↑	↑	↑	↑
C_2H_4	11.8	3.0	7.1	15.4	8.2				
C_3H_8	4.1	1.3	3.0	7.1	2.8	8.4	8.8	0.0	tr
C_3H_6	21.2	6.1	13.7	29.0	16.7				
C_4 .... [f)]	2.7	4.8	6.6	12.7	9.6	↓	↓	↓	↓
Others[g)]	4.5	3.7	2.0	6.3	2.2	tr	1.8	0.5	0.0

a) Yield(%) = 100 x flow rate (mol/hr) of a given product x carbon number in its molecular formular / feed rate (mol/hr) of methanol. Samples were analyzed at 1hr on stream. H_2O and H_2 were obtained as non carboneous products.

b) 10 wt% ($Al(H_2PO_4)_3$, $NiSO_4$) and 12 wt% ($ZnCl_2$) supported on Neo-bead DL-4. Catalyst 1 gram ≈ 2 cm^3.

c) Neo-bead DL-4 alone.

d) Yield(%) = 100 x CH_3OH (mol) in the liquid product (cumulation during 0~1 hr on stream) / CH_3OH (mol) fed (1hr).

e) Poor accuracy for the yield below 10 % because of the overlap of its gc curve with that of Ar.

f) Mainly C_4H_8. g) C_5 and CH_3Cl.

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