

Decomposition of Methanol to Syngas over AlPO_4 -Supported Nickel Catalyst

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An AlPO_4 -supported nickel catalyst exhibited significantly higher activity and selectivity for the title reaction than such conventional catalysts as $\text{Ni}/\text{Al}_2\text{O}_3$, Ni/SiO_2 , Ni/TiO_2 , and $\text{CuO-ZnO-Cr}_2\text{O}_3$. The effects of Ni loading and temperatures of reduction and reaction on its catalytic property were also investigated.

Recently, the existence of metal-support interaction on Ni/AlPO_4 has been inferred from kinetic behaviors of such catalyst during hydrogenation reactions.¹⁾ In addition, it has also been observed that Ni/AlPO_4 exhibits a suppression of its normal H_2 chemisorptive capacity when reduced at high temperatures, much as is observed in "SMSI" supports.²⁾ In spite of this suppression in hydrogen chemisorption, Ni/AlPO_4 has been reported to be highly active for liquid-phase hydrogenation reactions.¹⁾ Its high activity has, however, been revealed to be apparent or nominal one and to be caused by the open-pore structure, on the basis of the catalytic activity for gas-phase hydrogenation of benzene where no significant transport effects are present to confound the apparent activity with the real one.³⁾ Thus, there has been little or no study which evidently showed that Ni/AlPO_4 displayed significantly higher activity and selectivity than conventional supported-nickel catalysts. Very recently, we have found that Ni/AlPO_4 exhibited high activity and selectivity for the decomposition of methanol to syngas, toward which much interest has been directed because of its variety of applications: syngas for combustion in a motor engine,⁴⁾ syngas as source of chemicals, etc.

All catalysts used in this investigation were prepared to contain nominally 10% Ni, unless otherwise specified, by impregnating the corresponding supports with nickel nitrate solutions of appropriate concentrations. The impregnates were dried at 120 °C for 12 h, calcined at 400 °C for 2 h, and sized to 16-32 mesh prior to reduction. An AlPO_4 was precipitated by heating a solution consisting of aluminum nitrate, phosphoric acid, ammonium hydroxide, and urea at 90 °C for 3 h, followed by drying at 120 °C for 16 h, and calcining at 400 °C for 2 h. The TiO_2 -support used was prepared by the hydrolysis of titanium tetrakisopropoxide. Hydroxyapatite (HAp) was prepared following the method described by Urabe and Izumi.⁵⁾ Both Al_2O_3 (JRC-ALO4) and SiO_2 (JRC-SIO1) were offered by Catalysis Society of Japan. Methanol decomposition was conducted using an ordinary continuous flow apparatus. Each catalyst (0.10 g) was loaded into a reactor and then reduced at 500 °C for 2 h, unless otherwise stated, followed by a helium flush at the temperature of

reduction for 30 min. The feed rate was $43 \text{ cm}^3 \cdot \text{min}^{-1}$ for helium saturated with the vapor of methanol maintained at 10°C . The effluent gas was analyzed chromatographically using thermal conductivity detector with active carbon and triacetone columns.

The results obtained for methanol conversion over various nickel catalysts at 300°C were listed in Table 1.

The conversions and compositions shown in Table 1 and the subsequent Tables are those obtained at the steady state of the reaction unless otherwise noted. When AlPO_4 and HAp were used as catalyst supports, both activities and selectivities, which refer conversions and CO-compositions, respectively, were excellent. In contrast, considerable amount of CH_4 was produced over $\text{Ni}/\text{Al}_2\text{O}_3$, and rather lower activity was observed over Ni/SiO_2 although its selectivity was similar to that of Ni/AlPO_4 .

When the reaction was carried out at 400°C , all catalysts showed 100% conversions, the selectivities being much different from one another (Table 2). The selectivity of Ni/AlPO_4 was very similar to that observed in the reaction at 300°C , whereas remarkable amounts of CH_4 and CO_2 were formed over other catalysts. As is distinct from Ni/AlPO_4 , lower selectivity was found over Ni/HAp although both supports are classified into metal phosphates.

The relationship between nickel loadings in Ni/AlPO_4 catalysts and their activities or selectivities was examined. As seen in Table 3, the

Table 1. Methanol Decomposition at 300°C

Supports	Conversion	Composition /%			
	%	CO	CH_4	CO_2	DME
AlPO_4	99.4	97.6	2.4	0.0	0.0
Al_2O_3	97.5	84.7	14.3	0.0	0.0
SiO_2	80.1	97.0	3.0	0.0	0.0
HAp	97.6	94.4	5.6	0.0	0.0

Table 2. Methanol Decomposition at 400°C

Supports	Conversion	Composition /%			
	%	CO	CH_4	CO_2	DME
AlPO_4	100.0	95.5	4.5	0.0	0.0
Al_2O_3	100.0	4.0	63.8	32.2	0.0
SiO_2	100.0	25.7	44.4	29.9	0.0
HAp	100.0	63.3	23.3	13.4	0.0

Table 3. Methanol Decomposition over Ni/AlPO_4 with Different Ni Loading at 400°C ^{a)}

Loading	Conversion	Composition /%			
	%	CO	CH_4	CO_2	DME
0	81.4	0.0	0.0	0.0	100.0
5	97.0	62.3	3.8	0.0	33.9
10	100.0	95.5	4.5	0.0	0.0
20	100.0	81.5	13.5	5.0	0.0
30	100.0	67.9	20.1	12.0	0.0

a) Time on stream: 48 h, except for the catalyst with 30% loading (6 h).

composition of dimethyl ether (DME) decreased sharply with the rise in the loading while that of CH_4 or CO_2 increased gradually. The maximum selectivity was observed at 10% loading. This result suggests that an optimum interaction between nickel and the support is needed to result in good catalyst-performance.

Contrary to expectation, the catalytic property of Ni/AlPO_4 was not almost varied by the reduction temperature (Table 4) in spite of the existence of SMSI on Ni/AlPO_4 .

Table 5 shows the results obtained with various catalysts. It is noted that Ni/TiO_2 reduced at 600 °C exhibited less activity than that reduced at 500 °C. This will be explained by a SMSI effect, since TiO_2 is known to be a SMSI-support⁶⁾

Table 4. Methanol Decomposition over Ni/AlPO_4
Reduced at Various Temperatures

Reduction temperatures °C	Conversion %	Composition /%			
		CO	CH_4	CO_2	DME
400	100.0	92.6	6.8	0.6	0.0
500	100.0	95.5	4.5	0.0	0.0
600	100.0	94.0	4.0	0.0	2.0
800	100.0	92.4	3.9	0.0	3.7

Table 5. Methanol Decomposition over Various Catalysts

Catalysts	Reaction temperatures °C	Conversion %	Composition /%			
			CO	CH_4	CO_2	DME
Ni/TiO_2	300	10.0	72.3	0.0	0.0	27.7
	400	77.3	47.5	36.2	15.5	0.8
Ni/TiO_2 ^{a)}	400	16.3	98.6	1.4	0.0	0.0
$\text{Ni}/\text{AlPO}_4\text{-Al}_2\text{O}_3$ ^{b)}	250	86.1	0.0	0.0	0.0	100.0
	400	100.0	70.7	22.0	7.3	0.0
Ni/AlPO_4 ^{c)}	400	100.0	90.0	8.0	2.0	0.0
$\text{Ni}/\text{AlPO}_4\text{-5}$	300	99.8	96.2	3.8	0.0	0.0
	400	100.0	63.4	22.7	13.9	0.0
$\text{Ni}/\text{Al}_2\text{O}_3\text{-K}$ (Ni 4%, K 2%)	300	15.1	100.0	0.0	0.0	0.0
	400	99.1	90.6	3.1	6.3	0.0
$\text{CuO-ZnO-Cr}_2\text{O}_3$ (CCIFE-KMB)	300	43.0	95.6	1.4	3.0	0.0
	400	13.9	87.9	0.0	12.1	0.0

a) Reduced at 600 °C. b) Al/P=1.8. c) Cristobalite-form.

and in practice, the crystallite diameters of Ni/TiO₂ reduced at 500 and 600 °C were nearly equal (ca. 15 nm). The difference in catalytic property of Ni depending on the supports, AlPO₄ and TiO₂ suggests that mechanisms for SMSI are different with each other, as indicated by a magnetic study.⁷⁾ It is interesting that Ni/AlPO₄-Al₂O₃ (Al/P=1.8) is intermediate in catalytic feature between Ni/AlPO₄ and Ni/Al₂O₃. Instead of amorphous AlPO₄, a crystalline AlPO₄ (cristobalite-form) was also employed as a support. It was observed by a separate experiment that the solubility of amorphous AlPO₄ was about 5 times that of crystalline one. However, no difference in support feature was found between them. Therefore, the surface properties of AlPO₄-supported catalysts will be little affected by the existence of phosphate ion eluted from the supports during the impregnation process described above. The characteristic of AlPO₄-5 as a support, which is known to possess zeolite-like structure,⁸⁾ seems to resemble that of Al₂O₃ in the sense that nickel catalysts using both supports provide excellent selectivities at 300 °C of the reaction temperature but poor ones at 400 °C. Mizuno et al.⁹⁾ have shown that the selectivity of Ni/Al₂O₃ can be modified remarkably by adding potassium as an additive. For comparison the same catalyst was prepared and examined. However, Ni/AlPO₄ was superior in both activity and selectivity to Ni/Al₂O₃-K at 300 °C of the reaction temperature. A commercial catalyst, CuO-ZnO-Cr₂O₃, was also investigated, but its activity was lower than that of Ni/AlPO₄ on a catalyst-weight basis.

Consequently Ni/AlPO₄ is considered to be a promising catalyst for the conversion of methanol to syngas, although the nature of the interaction between Ni and AlPO₄ which remarkably modified the catalytic property of Ni for this reaction is not yet understood.

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