Methanol Conversion on Ni/SiO₂ and Ni/Al₂O₃ Catalysts

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The relationship between activity for catalytic conversion of methanol and the properties of Ni/SiO₂ and Ni/Al₂O₃ catalysts was studied. Syngas (2H₂+CO) was selectively produced by both catalysts up to the point at which *ca.* 87% of the input methanol was converted. As the reaction temperature was increased, methane was synthesized from the syngas produced by methanol conversion. This reaction was followed very closely by the shift reaction which yielded CO₂ and H₂ from the reaction of CO from the syngas and H₂O, the byproduct of the methane formation reaction. The apparent activation energy for formation of H₂ was 15 kcal/mol for Ni/SiO₂ and Ni/Al₂O₃ with Ni loading greater than 5 wt%. When Ni was less than 3 wt%, the catalytic activity of the Ni on the alumina support was considerably weakened by strong metal-support interactions, and the dimethyl ether formation on the acidic sites of the alumina support predominated over the syngas formation. Lanthanum oxide added to the Ni/Al₂O₃ catalyst suppressed the dimethyl ether formation with a resulting increase in the yield of H₂. In the case of Ni/SiO₂ catalyst, however, no metal-support interaction nor dimethyl ether formation was observed, and the lanthanum oxide did not affect the catalytic activity.

1. Introduction

Recently, a considerable degree of interest has been directed toward a variety of applications of methanol as a potential C₁ compound for production of gasoline and olefins over shape-selective zeolite catalysts. Other fundamental compounds, such as acetic acid, ethylene glycol, acetaldehyde, etc, could also be possible reactants for catalyzed syntheses from methanol. As inexpensive supplies of methanol become more readily available¹⁾ catalytic conversion of methanol to highly pure syngas or town-gas of high caloric value may become an important, economical source of energy.

In recent papers, Niiyama et al.²⁾ and Kasaoka and Shirakami³⁾ have described decomposition of methanol over various metals and metal oxides in which platinum group metal catalysts were found to be effective for selective decomposition of methanol to H₂ and CO. However, the relationship between catalysts' properties and their activity/selectivity for methanol conversion has not been studied extensively.

In our previous paper⁴⁾, nickel was found to be a favorable main catalyst component for successful decomposition of methanol to syngas. This study was undertaken to examine the relationship be-

tween the performance and the properties of nickel catalysts supported on SiO₂ or Al₂O₃ for methanol conversion. A convenient technique of CO-adsorption measurement by flow method was used to determine the surface area of the reduced nickel, although some papers, on use of CO-adsorption measurement by static method for determining the particle size of supported Ni have been reported^{5),6)}.

2. Experimental

2.1 Catalyst

Silica and alumina were used as support materials in this study. The silica support was MERCK 60~80 mesh (BET-surface area, 465 m²/g; porosity, 62.0%; bulk density, 0.49 g/cm³) previously washed with aqua regia and calcined at 500°C for 5 hr. The alumina support was γ -Al₂O₃[†] precalcined at 700°C (BET-surface area, 177 m²/g; porosity, 68.0%; bulk density, 0.90 g/cm³)⁷⁾. Nickel catalysts supported on silica or alumina were prepared by the incipient wetness technique with a Ni(NO₃)₂ solution containing the desired nickel concentration. For example, 7.5 wt% Ni/SiO₂ catalyst was prepared by impregnating the pores of SiO₂ support with a 18 wt% Ni(NO₃)₂ solution. After impregnation, the samples were dried in air for 2 hr at room temperature, followed by heating at 110°C for 2 hr. The dried samples were then heated in

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air to form nickel oxide, followed by reduction in a hydrogen stream at 500°C for 1 hr. The reduced catalysts were stocked in glass ampoules. Before each run the catalyst was reduced *in situ* with a stream of 10% H₂ + 90% N₂ at 400°C for 10 min to reduce the Ni surface which was partly oxidized by air during the packing of the catalyst into the reactor. A fresh batch of catalyst was used for each run.

2.2 Apparatus and Procedure

Kinetic measurements of methanol decomposition were performed in an ordinary continuous flow apparatus as previously described⁸). Briefly, a 0.30 g portion of the catalyst was packed into the reactor equipped with a methanol evaporator. The reaction was carried out by raising the temperature of the catalyst bed to 430°C at a constant rate of 2°C/min. The effluent gas was analyzed chromatographically using thermal conductivity and flame ionization detectors with MS-5A and Porapak-T columns.

The specific metal-surface areas of supported nickel catalysts were determined by the CO adsorption technique using a pulse method as previously described⁸). The reduced nickel surface area, S (m²/g-Ni), and the average particle size, $\bar{d}$ (nm) were calculated by the following equations assuming that the cross-sectional area of the adsorbed CO molecules is 13.0 Å²⁹) and all nickel particles were spheres.

$$S = 7.83 \times 10^4 \times a, \quad \bar{d} = \frac{6}{\rho \cdot S}$$

where a is the amount of CO adsorbed (mol/g-Ni) and ρ is the specific gravity of nickel.

3. Results and Discussion

3.1 Temperature Dependence

A typical example of the temperature dependence of methanol conversion and space-time yields (Y^{ST}) for each product over a Ni/SiO₂ catalyst is shown in **Fig. 1** together with the reaction conditions. The value of Y^{ST} of H₂ and CO increased up to about 320°C at which point methanol conversion had reached about 87%; the formation of methane and CO₂ was observed above this temperature (**Fig. 1**). From the temperature dependence of the product distribution, the following reaction pathways were considered for conversion of methanol over Ni/SiO₂ catalysts:

Fig. 1 Temperature Dependence of Space-Time Yield for Each Product and Methanol Conversion

On the other hand, when Ni/Al₂O₃ catalysts were employed, considerable amounts of dimethyl ether and water, in addition to H₂ and CO, were formed at relatively low temperatures according to Eq. (4), particularly with low Ni loadings.

The formation of dimethyl ether was attributed to the acidic properties of the Al₂O₃ support as reported previously⁸). The effects of temperature on the value of Y^{ST} for H₂ over Ni/SiO₂ catalysts with nickel loadings of 1.9, 7.5, 15.2, and 22.6 wt% are shown in **Fig. 2**. Arrhenius-type plots (**Fig. 2**) were parallel for all catalysts up to 20% methanol conversion. The apparent activation energy was 15.1 kcal/mol. For Ni/Al₂O₃ catalysts, the appar-

Ni Loading (wt%);
○ : 22.6, □ : 15.2, △ : 7.5, ● : 1.9

Fig. 2 Effect of Temperature on the Space-Time Yield of H₂ on Ni/SiO₂

ent activation energy was 14.6 kcal/mol for 9.3, 7.3, and 5.1 wt% Ni and 31.9 kcal/mol for 3.1, 1.9, and 0.8 wt% Ni as shown in **Fig. 3**. These results are discussed below.

The effect of contact time on activity and selectivity for methanol conversion was then examined. When a 7.5% Ni/SiO₂ catalyst was employed at 400°C, syngas was selectively formed during very short contact times, below 0.06 sec, or until about 50% of the methanol had been converted (**Fig. 4**). The production of methane and CO₂ increased rapidly according to Eqs. (2) and (3), as methanol conversion proceeded beyond 50%. From these results, it was concluded that lower contact times, higher space velocities, would be suitable for syngas formation. However, longer contact periods were required for town-gas production over Ni/SiO₂ catalysts (**Fig. 4**).

Fig. 3 Effect of Temperature on the Space-Time Yield of H₂ on Ni/Al₂O₃

Fig. 4 Effect of Contact Time on Methanol Conversion and Product Distribution
Catalyst : 7.5% Ni/SiO₂, Temperature : 400°C

3.2 Effect of Nickel Loading and the Kind of Support

The CO adsorption on supported Ni catalysts has been extensively studied^{5),10)} as a means of estimating the specific surface area, dispersion, and average particle size of Ni. Bartholomew et al.⁵⁾ investigated CO adsorption on Ni/Al₂O₃, Ni/SiO₂, and Ni/TiO₂ catalysts and reported that Ni/SiO₂ showed but slight interaction between Ni and SiO₂, but Ni/Al₂O₃ had a strong metal-support interaction (SMSI). Smith et al.¹⁰⁾ reported in a recent paper that good agreement among H₂, CO, and O₂ chemisorptions, XRD, and TEM techniques for determining Ni particle size was obtained for Ni/SiO₂ and Ni/Al₂O₃ catalysts. In this study, the CO adsorption technique that was used to calculate copper particle size in our previous paper⁸⁾ was used to estimate the surface area of reduced Ni.

3.2.1 Ni/SiO₂ Catalysts

The results of CO adsorption measurements on Ni/SiO₂ catalysts are presented in **Table 1**. CO uptake increased approximately in proportion to Ni loading, and the average particle size ($\bar{d}$, nm) showed a slight increase with Ni loadings less than about 10 wt%, and nearly constant with greater loadings. **Fig. 5** shows the effects of Ni loading on the Y^{ST} and Y^{AT} values (moles of product per unit surface area of nickel per unit time) of products. H₂ and CO were formed at a ratio of 2/1

Table 1 CO Adsorption for Various Ni/SiO₂ Catalysts with Different Ni Loadings

Ni Loading (wt%)	CO Uptake (μ moles/g)	S (m ² /g-Ni)	$\bar{d}$ (nm)
1.9	16.8	69.4	9.7
3.4	26.2	60.4	11
7.5	68.4	71.9	9.4
12.0	94.6	62.0	11
15.2	122	62.8	11
19.3	154	62.8	11
22.6	161	55.9	12

Fig. 5 Effect of Ni Loading of Ni/SiO₂ Catalysts on the Formation Rates of H₂ and CO
Temperature : 200°C

according to Eq. (1), and the value of Y^{ST} is regarded as the formation rate of products. On the contrary, Y^{AT} decreased with increasing Ni loading up to 10 wt% and was almost constant for greater than 10 wt% Ni. These results show that methanol conversion to syngas over Ni particles supported on SiO_2 is structure-sensitive in the range of lower Ni loadings and is structure-insensitive in the range of higher Ni loadings. Furthermore, it is suggested that the metal-support interaction is considerably weak for Ni/ SiO_2 catalysts for the following reasons. (i) If a strong interaction, such as formation of nickel silicate, exist, it would be expected that Y^{ST} is very small in the range of lower Ni loadings due to the decrease in the reduced Ni surface area.

However, the fact seen in **Fig. 5** shows an increase in Y^{ST} with increasing Ni loading in the range of lower Ni loadings (1.9~7.5 wt%). (ii) In our previous paper¹¹⁾ the Ni particle size in the 5 wt% Ni/ SiO_2 catalyst obtained from CO adsorption (14.6 nm) was almost the same as that estimated from X-ray diffraction measurement (14.3 nm). The result that Ni-silica interaction is considerably weak is similar to that reported by Bartholomew et al.⁵⁾ and by Smith et al.¹⁰⁾.

3.2.2 Ni/ Al_2O_3 Catalysts

Carbon monoxide adsorption data on Ni/ Al_2O_3 catalysts are presented in **Table 2**. CO uptake increased with increasing Ni loading. The activities for various Ni/ Al_2O_3 catalysts with different Ni loadings are shown in **Fig. 6**. Dimethyl ether and water were produced at 200°C on catalysts with less than 3 wt% Ni loadings, and at higher, H_2 and CO formation increased with increasing Ni loading. This indicates that when Ni loading is low, the catalytic activity of the Ni in Ni/ Al_2O_3

Fig. 6 Effect of Ni Loading of Ni/ Al_2O_3 Catalysts

catalysts is weakened by strong NiO- Al_2O_3 interactions such as the formation of a NiAl_2O_4 ¹²⁾ and/or by the decrease in methanol concentration due to dimethyl ether formation on the Al_2O_3 support.

Lanthanum oxide was added to Ni/ Al_2O_3 catalysts in an atomic ratio of Ni/Al=5/1^{4),11)} in order to reduce the acidity of Al_2O_3 . As a result, dimethyl ether and water were not formed at all, and the increase in the value of $Y_{\text{H}_2}^{ST}$ was as shown in **Fig. 7** about twice the value for $Y_{\text{H}_2}^{ST}$ when lanthanum oxide was not used. These results indicate that acidity of Al_2O_3 support was weakened by the addition of basic La_2O_3 resulting in the decrease in dimethyl ether formation on the Al_2O_3 support. For Ni/ SiO_2 catalysts only a little enhancement of $Y_{\text{H}_2}^{ST}$ values was observed by the addition of lanthanum oxide (**Fig. 7**).

To investigate the effect on the reaction rate of Ni surface area with the same level of Ni loading, catalysts were prepared by calcining 5.3 wt% Ni/ Al_2O_3 in air at 300, 400, 500, 600, and

Table 2 CO Adsorption for Various Ni/ Al_2O_3 Catalysts with Different Ni Loadings and Calcination Temperatures

Ni Loading (wt%)	CO Uptake (μ moles/g)	S ($\text{m}^2/\text{g-Ni}$)
0.8	2.75	26.9
1.9	6.44	26.0
3.1	20.5	51.7
5.1	45.8	70.0
7.3	88.8	95.6
9.3	97.8	83.0
5.3 ^{a)} (300°C)	55.9	83.3
5.3 ^{a)} (400°C)	52.6	78.5
5.3 ^{a)} (500°C)	45.7	67.9
5.3 ^{a)} (600°C)	36.0	53.6
5.3 ^{a)} (700°C)	8.44	12.6

a) The catalyst was calcined at the temperature represented in parentheses for 3 hr and again reduced at 500°C for 15 hr.

Fig. 7 Effect of Lanthanum Oxide Added to Ni/ Al_2O_3 and Ni/ SiO_2

Fig. 8 Effect of Calcination Temperature on the Catalyst Performance of Ni/Al₂O₃

700°C, for 3 hr followed by H₂ reduction at 500°C. The CO adsorption data for the calcined catalysts are presented in **Table 2**. The surface of the reduced Ni decreased with increasing calcination temperature, especially above 500°C. The decrease in the Ni surface area is probably attributed to the sintering of the Ni particles. The influence of calcination temperature of catalyst on methanol decomposition is shown in **Fig. 8**. Yields of H₂ and CO per surface area of reduced Ni (Y^{AT}) increased with increasing calcination temperature in the range of 300~600°C, while they decreased on the catalyst calcined at 700°C. Y^{AT} for dimethyl ether, which shows m mol of dimethyl ether formed per reduced Ni surface area per hour, was increased remarkably above 600°C. On the other hand, Y^{ST} for dimethyl ether was almost constant below 500°C and increased only to a small extent above that temperature.

The change in Y^{AT} of products with changing calcination temperature can be interpreted as follows. The sintering of Ni particles calcined below 500°C is considered to be of minor effect, since the catalysts used here were pretreated at 500°C, and Y^{ST} of dimethyl ether did not change. Hence, the increase in Y^{AT} of products is probably due to the decrease in the Ni surface area caused by spinel formation. On the other hand, above 600°C, Y^{AT} of syngas decreased markedly, and both Y^{ST} and Y^{AT} of dimethyl ether increased. In this tem-

perature range, the increase in Y^{ST} of dimethyl ether was due to the exposure of the acidic alumina surface area brought about by the sintering of Ni particles.

4. Conclusion

(1) During the catalytic conversion of methanol on supported Ni catalysts, the selective formation of syngas was observed at as low temperature as 320°C, corresponding to 87% methanol conversion, whereas with increasing temperature there was an increase in hydrogenation of CO and in shift reaction between CO and H₂O leading to the formation of methane and CO₂.

(2) The catalytic properties of Ni were significantly affected by the kind of support (SiO₂ and Al₂O₃) used. The catalytic activity of Ni supported on Al₂O₃ for syngas formation was weakened by a strong metal-support interaction (SMSI) such as the formation of a NiAl₂O₄ spinel and/or the decrease in methanol concentration due to dimethyl ether formation on the acidic sites of Al₂O₃ support. The acidity of Al₂O₃ was decreased considerably by the addition of La₂O₃ resulting in a higher activity. On the other hand, SiO₂ support showed no SMSI and it did not produce dimethyl ether; and the addition of La₂O₃ had no effect on syngas formation.

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要 旨

シリカおよびアルミナ担持ニッケル触媒によるメタノールの接触変換

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今後、メタノールの供給が増大することが予想される¹⁾が、それに伴ってメタノールを接触変換して高純度の合成ガスあるいは高熱量の都市ガスを得る課題が重要になると考えられる。しかし、これらの課題についての今までの研究例^{2),3)}は少なく、しかも触媒探索の段階であって、詳しい研究は行われていない。

著者らは、前報⁴⁾でメタノールからの合成ガス生成反応に Ni 系触媒が有効であることを示したが、本研究ではシリカおよびアルミナ担持 Ni 触媒のメタノール転化性能と Ni 触媒の性質との関連について検討した。

Ni/SiO₂ 触媒の場合、メタノール濃度 30%，空間速度 5,000 hr⁻¹ の条件で、約 320°C (メタノール転化率 87%) 以下ではほぼ選択的 (H₂/CO=2/1) に合成ガスが生成し、それ以上の温度では主としてメタンと CO₂ が生成した (Fig. 1)。これらの生成物はそれぞれ Eqs. (1)~(3) に従って生成したと考えられる。アルミナ担体の場合には、ジメチルエーテルも生成した。これは Eq. (4) で示されるメタノールの脱水縮合反応がアルミナの酸性点上で起こったものと考えられる。

H₂ の生成速度に対するみかけの活性化エネルギーは 15 kcal/mol であった (Figs. 2 と 3)。また、反応温度 400°C における接触時間の影響を調べた結果、接触時間 0.06 sec 以下 (メタノール転化率 50% 以下) で合成ガスが選択的に生成し、0.25 sec 以上ではメタノール転化率は 100% となり、都市ガス生成に適することがわかった (Fig. 4)。

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つぎに、Ni 担持量のメタノール分解反応に及ぼす影響をシリカおよびアルミナ担体を用いて調べた。シリカ担持 Ni 触媒への CO 吸着 (Table 1) より、Ni 粒径は Ni 担持濃度が 10 wt% 以下では、担持量の増加とともにわずかに増したが、それ以上の担持濃度ではほぼ一定であった。また単位触媒体積あたりの活性 (YST) は担持濃度の増加とともに増したが、単位 Ni 表面積あたりの比活性 (Y^{AT}) は Ni 担持濃度が増すと 10 wt% 以下では減少し (structure-sensitive), 10 wt% 以上ではほぼ一定であった (structure-insensitive) (Fig. 5)。一方、アルミナ担体では Ni 濃度が 3 wt% 以下の範囲で H₂ の生成は全く認められず、Ni 濃度が増すにつれて Y^{AT}_{H₂}, YST_{H₂} ともに増加した (Fig. 6)。このことから、アルミナ担持 Ni 触媒では Ni と担体のアルミナとの間に、シリカ担体では認められなかった強い相互作用 (たとえば NiAl₂O₄ の形成⁵⁾) の存在が示唆され、同時にアルミナ酸点上でのジメチルエーテルの生成によるメタノール濃度の減少のため Ni の合成ガス生成に対する触媒活性が弱められることが考えられた。さらに、塩基性の酸化ランタンを両触媒に添加すると、アルミナ担体ではジメチルエーテルの生成が減少し、H₂ 生成速度は約 2 倍に増加したが、シリカ担体の場合には顕著な効果は観測されなかった (Fig. 7)。アルミナ担持 Ni 触媒の焼成温度の影響を調べたところ、Y^{AT}_{H₂} は焼成温度の増大とともに増したが、600°C 以上の焼成温度では逆に Y^{AT}_{H₂} は減少した。600°C 以上では、Ni 表面は Ni 粒子のシンタリングにより著しく減少し、そのため露出したアルミナ表面でのジメチルエーテル生成量が増すことによって、H₂ と CO の生成が減少したと考えられた。また、600°C 以下までの Y^{AT} の増加傾向は触媒があらかじめ 500°C 処理済みであることから、シンタリングが原因とは考えにくく、スピネル形成による Ni 表面の減少に基づくと思われる。

Keywords

Metal support interaction, Methanol conversion, Nickel alumina catalyst, Nickel concentration, Nickel silica catalyst