Synthesis of Acetonitrile from Syngas and Ammonia over Silica-supported Molybdenum Catalysts Modified by Silver

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Direct synthesis of acetonitrile from syngas and ammonia over silica-supported molybdenum catalysts was studied. The catalysts were prepared by impregnation of silica followed by calcination and reduction. The reduction treatment in the preparation, however, had little influence on the activity of Mo/SiO₂, because the reduction of Mo species on silica proceeds under the reaction atmosphere. Ag had an excellent effect on the catalyst to improve its activity and selectivity to acetonitrile. The optimum reaction temperature was between 450°C and 500°C. The weight change of Mo/SiO₂ and Mo-Ag/SiO₂ during reduction treatment suggested that MoO₂ is the supported Mo species, regardless of whether Ag is added as a promoter or not. From the X-ray diffraction measurements, it was speculated that MoO₂ is the active species for the formation of acetonitrile and that Ag has an effect of making MoO₂ amorphous or more dispersed. The deactivation of the catalysts may be caused by both crystal growth of MoO₂ and surface fouling.

1. Introduction

It is well known that hydrogenation of carbon monoxide gives various hydrocarbons and oxygenated compounds. Numerous studies have been made on this reaction because it is a principal reaction in C₁ chemistry. C₁ chemistry including heteroatoms other than oxygen (e.g. nitrogen), however, has not received much attention until recently, in spite of its importance.

In 1949, Ruhrchemie¹⁾ got a patent to synthesize aliphatic primary amines by the addition of 0.5—5% ammonia to a FT reaction system with Fe catalysts. In 1973, W. R. Grace and Co.²⁾ secured a patent to prepare N-alkylamines by reaction of syngas and ammonia over Fe catalysts modified by Group IA, IIA, and III metals. Henrici-Olive and Olive³⁾ investigated this reaction and concluded that these amines are formed through dissociation of alkyl-metal bond by ammonia. They also proposed a possible reaction mechanism of FT synthesis. Other patents concerning the synthesis of nitrogen-containing compounds from syngas and ammonia include the preparation of trimethylamine with Cu-Cr catalysts,⁴⁾ acetamide with Rh-Mn catalysts,⁵⁾ and methylamine and ethylamine with Rh-Fe cat-

alysts.⁶⁾

Recently, Monsanto Co. got a patent for the preparation of acetonitrile from syngas and ammonia by using molybdenum catalysts.^{7),8)} This patent is significant in that this method gives nitrogen-containing C₂ compounds directly from carbon monoxide, hydrogen, and ammonia. Acetonitrile is useful as the starting material of medicines, perfumes and so on. Acetonitrile, moreover, can be converted to acrylonitrile by the reaction with formaldehyde,⁹⁾ with methane and oxygen,¹⁰⁾ or with methanol and oxygen.¹¹⁾ This suggests the possibility of the production of acrylonitrile from C₁ compounds.

No academic studies on this reaction, however, have been reported so far and details of this reaction are not clear. In this study, we have investigated the activity of modified molybdenum catalysts and found that silica-supported molybdenum-silver catalysts have positive activity for the formation of acetonitrile from syngas and ammonia. The effect of silver as a promoter was studied together through characterization of the catalysts.

2. Experimental

2.1 Preparation of Catalysts

The catalysts were prepared by simultaneous im-

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pregnation of silica (Davison #57, 8–12 mesh, surface area: 300 m²/g) with aqueous solutions of metal salts (eg. (NH)₄Mo₇O₂₄·4H₂O for Mo, chlorides for noble metals, and nitrates for other metals), and dried with a rotary evaporator (80°C 1 h, 110°C 1 h). The samples were then calcined by air at 500°C for 5 h, and usually reduced by passing hydrogen at 500°C for 3 h.

2.2 Reaction Procedures

The reactions were carried out with a continuous flow reaction system at atmospheric pressure. The reactor made of Pyrex was placed in a vertical furnace. The catalyst was reduced at 500°C for 1 h before reaction. The temperature was then changed to the reaction temperature and a mixture of CO, H₂, NH₃, and Ar (as the internal standard for analysis) was fed from cylinders at a rate of 13.6, 6.7, 25.0, and 9.8 cm³·min⁻¹, respectively. NH₃ from a cylinder was dried through a KOH column. Effluent gas was analyzed with gas chromatographs every 30 min by sampling with a preheated gas syringe.

The columns used were as follows: 2 m column, molecular sieve 5A, operating at 55°C for the analysis of CO, CH₄, and Ar; 3 m column, 1.5% squalane/activated charcoal, operating at 55°C for analysis of CO and CO₂; 3 m column, VZ-10, operating at 45°C for the analysis of hydrocarbons; 2 m column, amipak 124, operating at 65°C for the analysis of acetonitrile, CH₄, and other nitrogen-containing compounds.

The conversion, yield, and selectivity were defined as follows:

$$\text{Conversion (\%)} = \frac{\text{CO fed (mol)} - \text{CO recovered (mol)}}{\text{CO fed (mol)}} \times 100 \quad (1)$$

$$\text{Yield (\%)} = \frac{\text{Product produced (mol)} \times \text{Carbon number}}{\text{CO fed (mol)}} \times 100 \quad (2)$$

$$\text{Selectivity (\%)} = \frac{\text{Product yield (\%)}}{\text{Conversion (\%)}} \times 100 \quad (3)$$

2.3 Analysis of Catalysts

Fresh and used catalysts were identified by using an X-ray diffractometer (Philips, Model PW-1700). Oxidation state of supported metals was analyzed

by an X-ray photoelectron spectrometer (Shimadzu Mfg., Model ASIX). In this XPS experiment, Si2p peak of the silica support was used as the reference peak. A thermobalance (Cahn, Model RG) was also used to get information on the weight change of the catalysts during preparation.

3. Results and Discussion

3.1 Activity of Mo/SiO₂ Catalysts

Monsanto's patent states the use of silica-supported Mo and Fe catalysts for the synthesis of acetonitrile from CO, H₂, and NH₃. In a preliminary experiment, we found that silica-supported Mo and Fe are quite effective for acetonitrile formation. Group VIII metals other than Fe gave only hydrocarbons and CO₂. Since Mo was more active than Fe, we focused our attention on Mo/SiO₂ catalysts.

First, three Mo/SiO₂ catalysts (Mo 10%) were prepared by changing the conditions of preparation, and their catalytic activity was measured. Products were acetonitrile, hydrocarbons (mainly CH₄), CO₂, and traces of propionitrile. Judging from the carbon material balance, there ought to have been other products of small yields, but we did not detect other compounds such as amines. **Table 1** summarizes the results of reaction using the three catalysts. It is noted that there is not much difference in the activity among the three catalysts. To examine the reason, X-ray diffraction was measured for fresh and used catalysts. As can be seen from **Fig. 1**, Catalyst A, which has not been reduced with H₂, shows the pattern of MoO₃ before reaction, and the peaks of Catalyst B correspond to those of MoO₂. This indicates that Mo is reduced from MoO₃ to MoO₂ by reduction with H₂. The diffraction peaks of Catalyst C, which has been reduced with NH₃ instead of H₂, are not so clear, although the pattern seems to be that of molybdenum nitrides.

In spite of the differences in diffraction patterns before reaction, both Catalyst A and B showed the pattern of MoO₂ after being used in 1 h reaction. It is concluded, therefore, that Mo exists as MoO₂ in the working state, regardless of whether the

Table 1 Activity* of Mo/SiO₂ Catalysts

Catalyst	Conditions of Preparation	CO Conversion (%)	Selectivity (%)						
			CH ₃ CN	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	CO ₂
A	Calcination only	16.1	26.4	1.6	0.06	0.12	tr	tr	50.9
B	Calcination and Reduction with H ₂ (500°C, 3 h)	15.5	28.8	2.5	0.13	0.26	tr	0.06	48.9
C	Calcination and Reduction with NH ₃ (500°C, 10 h)	15.3	26.1	1.2	tr	0.06	tr	tr	50.1

* Reaction temperature : 450°C, Catalyst : Mo/SiO₂ (Mo 10%) 3 cm³. The data were obtained at 1 h on stream.

○ : MoO₃, △ : MoO₂, ◇ : Mo nitrides
Catalyst A, B, and C are listed in Table 1.

Fig. 1 X-Ray Diffractograms of Mo/SiO₂ Catalysts

catalyst is reduced or not before use. This is probably the reason why little difference in activity was observed between the two catalysts. In fact, a slight increase in the yield of acetonitrile with time on stream was observed with Catalyst A, in the early stage of the reaction. This may be explained by the reduction of MoO₃ to active MoO₂ species under the reaction atmosphere. In contrast, the yield decreased monotonously with time on stream with Catalyst B.

In the case of Catalyst C, MoO₂ peaks were not observed after use, and yet it had almost the same catalytic activity as Catalyst A and B. The reason is not clear. One possibility is that MoO₂ is in

amorphous or highly dispersed state, as in the case of Mo-Ag/SiO₂ catalysts, which will be stated later. Another is that molybdenum nitrides are also active species.

3.2 Activity of Mo/SiO₂ Catalysts Modified with Other Metals

In order to improve catalytic activity, series of silica-supported Mo-containing bimetallic catalysts (Mo 5%) were prepared by simultaneous impregnation method. The results of reaction are given in Table 2.

The addition of alkali and alkaline earth metals to Mo/SiO₂ resulted in the decrease of CO conversion and selectivity to acetonitrile. The Group VIII metals have no beneficial effect, although Rh improves the selectivity to a little degree. On the other hand, Ag shows a striking effect as a promoter because the selectivity to acetonitrile is increased by about 50%. Our experiments also indicate that Cu improves the selectivity from 35 to 40%. While it is known that Cu is a good promoter,⁷⁾ there has not been a report yet on the prominent effect of Ag.

3.3 Effect of Ag as a Promoter

In order to elucidate the effect of Ag, Mo-Ag/SiO₂ catalysts having different Ag/Mo molar ratios were prepared. The Mo loading was fixed at 10 wt%. The activity of these catalysts is shown in Fig. 2. The CO conversion, acetonitrile yield, and the selectivity to acetonitrile all increased as the Ag/Mo ratio was increased from 0 to 0.2. No increase in activity, however, was observed beyond Ag/Mo = 0.2, showing that a small amount of Ag suffices to improve the catalytic performance. The same effect was also observed when Mo loading was 5 wt%.

3.4 Effect of Reaction Conditions

The effect of reaction temperature on Mo-Ag/SiO₂

Table 2 Activity*1 of Mo/SiO₂ Catalysts Modified with Other Metals

Catalyst*2	CO Conversion (%)	Selectivity (%)						
		CH ₃ CN	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	CO ₂
Mo	23.2	35	4.0	0.30	0.43	0.04	0.17	47
Mo-Li	20.4	26	2.0	0.10	0.15	tr	tr	6.5
Mo-Na	17.1	23	1.3	0.06	0.12	tr	tr	15
Mo-K	13.7	15	0.4	tr	tr	tr	tr	43
Mo-Rb	14.4	17	0.4	tr	0.07	tr	tr	42
Mo-Cs	15.8	13	0.4	tr	tr	tr	tr	33
Mo-Mg	17.9	23	1.6	0.06	0.17	tr	tr	32
Mo-Ca	19.0	31	2.6	0.16	0.26	tr	tr	38
Mo-Co	20.2	21	2.6	0.30	0.79	0.05	0.30	—
Mo-Ni	45.8	12	23	3.43	1.51	0.48	1.14	—
Mo-Ru	16.1	25	2.6	0.12	0.37	tr	tr	42
Mo-Rh	25.4	38	14	2.72	0.91	0.36	0.47	33
Mo-Cu	20.9	40	3.9	0.29	0.53	tr	tr	26
Mo-Ag	25.9	45	6.6	0.70	0.89	0.12	0.39	40
Mo-Au	14.0	18	1.9	0.07	0.29	tr	tr	57

*1 Reaction temperature : 450°C, Catalyst amount : 15cm³. The data were obtained at 3 h on stream.

*2 Mo 5 wt%, M/Mo (molar ratio) = 1/3 (Na/Mo = 1/10).

Fig. 2 Effect of Ag as a Promoter

Fig. 3 Effect of Reaction Temperature

(Mo 5%, Ag/Mo=1/7) is shown in **Fig. 3**. The reaction data were collected after stabilizing the catalyst by conducting a reaction for 22 h. It can be seen that acetonitrile yield reached a maximum at about 450°C, whereas hydrocarbons were formed in high yields as the reaction temperature was increased. Moreover, high temperature caused the decomposition of NH₃ producing a great amount of N₂. From these observations, it is concluded that the optimum reaction temperature is between 450°C and 500°C.

It is often possible to speculate reaction intermediates by examining the variation of product yields with reaction time. The effect of contact time is

Fig. 4 Effect of Contact Time

shown in **Fig. 4**. Within the range of contact time of 7 s, the yield of acetonitrile increased proportionally with contact time. While methylamine has been suspected to be the reaction intermediate because the conversion of methylamine to acetonitrile is known,¹²⁾ we could not detect any other nitrogen-containing products over the whole range of contact time. **Figure 4** also shows the higher activity of Mo-Ag/SiO₂ as compared to that of Mo/SiO₂.

3.5 Characterization of Catalysts

To elucidate the chemical state of Mo in the catalysts, the weight changes of the catalysts resulting from reduction treatment in the preparation were measured. A sample of about 0.4 g, impregnated and then calcined, was put in a thermobalance and the weight change by reduction with flowing hydrogen at 500°C for 3 h was recorded. The weight loss measured was 3.13 mg for Mo/SiO₂ (Mo 5%) and 2.98 mg for Mo-Ag/SiO₂ (Mo 5%, Ag/Mo=3/100). The calculated weight losses based on the assumption that Mo and Ag are in the form of MoO₃ and Ag₂O before reduction, and in the form of MoO₂ and Ag metal after reduction, were 3.13 mg for Mo/SiO₂ and 3.19 mg for Mo-Ag/SiO₂. As the agreement between the calculated and experimental values is quite satisfactory, it is evident that Mo exists as MoO₂ after reduction, regardless of whether Ag is added as a promoter or not. Thus no difference in the oxidation state of Mo was observed between Mo/SiO₂ and Mo-Ag/SiO₂.

The oxidation state of Mo at the surface was analyzed by X-ray photoelectron spectroscopy. The binding energy was corrected based on the

a : Mo/SiO₂ (Mo 5%),
b : Mo-Ag/SiO₂ (Mo 5%, Ag/Mo=3/100)

Fig. 5 XPS Spectra of Mo/SiO₂ and Mo-Ag/SiO₂ in the Mo3d Region

○ : MoO₃, □ : Ag₂MoO₄
The samples have been impregnated and calcined by air at 500°C for 5 h.

Fig. 6 X-Ray Diffractograms of Mo-Ag/SiO₂ Catalysts (Mo 10%) after Calcination

Si2p reference peak (103.6 eV). **Figure 5** indicates that surface Mo is a mixture of Mo(VI) and Mo(IV) in both Mo/SiO₂ and Mo-Ag/SiO₂. It might be seen that the intensity of Mo(IV) is a little greater for Mo-Ag/SiO₂, which is not so convincing. The catalyst samples in this measurement were reduced in situ within the XPS chamber at 300°C for 1 h, and yet there is no guarantee that the reduction would be complete. Thus, no useful information on the effect of Ag was obtained.

X-ray diffractograms of a series of Mo-Ag/SiO₂ catalysts (Mo 10%) during the preparation are shown in **Figs 6, 7, and 8**. In **Fig. 6** showing the diffractograms after calcination, the peaks cor-

△ : MoO₂, ● : Ag metal, ▽ : Mo metal
The samples have been impregnated, calcined, and reduced by hydrogen at 500°C for 3 h.

Fig. 7 X-Ray Diffractograms of Mo-Ag/SiO₂ Catalysts (Mo 10%) after Reduction

responding to MoO₃ are observed when Ag/Mo is less than 1/7 and that the pattern of Ag₂MoO₄ is observed instead of that of MoO₃ when the amount of Ag is more than that value. Small peaks other than those of Ag₂MoO₄ also appear, although the assignment is unknown. These observations suggest that mixed oxides from Mo and Ag are formed by the calcination.

Figure 7 indicates the diffractograms after reduction following calcination. Mo/SiO₂ shows the pattern of MoO₂. It should be noted, however, that the peaks of MoO₂ are replaced by those of Mo and Ag metals when Ag is added to Mo/SiO₂. This suggests that Ag has the effect of promoting the reduction of Mo to the lower oxidation state. Nevertheless, it is unreasonable, from the thermobalance experiments, to assume that all of the Mo atoms in Mo-Ag/SiO₂ are in the form of Mo metal. Probably, most of the Mo atoms exist as MoO₂ in amorphous or highly dispersed state in the presence of Ag promoter. It may be speculated, therefore, that MoO₂ is the active species for the conversion of syngas and NH₃ to acetonitrile, and that Ag makes MoO₂ amorphous or highly dispersed. This conclusion is supported by X-ray diffractograms in **Fig. 8**, showing that the peaks of MoO₂ replace those of Mo metal rapidly during the reaction. Diffractograms in **Fig. 8** further show that the intensity of MoO₂ peaks of Mo/SiO₂ is larger than

△ : MoO₂, ● : Ag metal

The samples have been used as catalysts for 1 h at 450°C.

Fig. 8 X-Ray Diffractograms of Mo-Ag/SiO₂ Catalysts (Mo 10%) after Use

those of Mo-Ag/SiO₂.

3.6 Deactivation of Catalysts

The change in catalytic activity of Mo/SiO₂ (Mo 5%) and Mo-Ag/SiO₂ (Mo 5%, Ag/Mo=3/100) with time on stream is shown in Fig. 9. The activity deteriorates gradually with time. The X-ray diffractogram of Mo/SiO₂ indicates the appearance of MoO₂ peaks after reaction of 28 h, though no diffraction peaks are detected for fresh Mo/SiO₂. This variance suggests the relationship between the catalyst deactivation and the appearance of MoO₂ diffraction peaks, namely, the growth of MoO₂ crystals.

With respect to the difference in the activity observed between Mo/SiO₂ and Mo-Ag/SiO₂, Fig. 9 serves to show that the activity of the latter is higher than that of the former in the early stage of reaction. With time on stream, however, the difference diminishes. As no diffraction peaks cor-

○ : Mo/SiO₂ (Mo 5%),

● : Mo-Ag/SiO₂ (Mo 5%, Ag/Mo=3/100)

Reaction temperature : 450°C, Catalyst amount: 15 cm³

Fig. 9 Variation of Catalytic Activity with Time on Stream

responding to MoO₂ was observed for Mo-Ag/SiO₂ after reaction of 28 h, the crystal growth of MoO₂ is probably not the sole factor of catalyst deactivation.

The regeneration of the catalysts by reduction at 500°C for 3 h was partially successful. As no change in the X-ray diffractograms were observed, surface fouling may be one of the factors of catalyst deactivation. This might explain the small difference in activity between Mo/SiO₂ and Mo-Ag/SiO₂ after reaction of 28 h, in spite of the difference in the X-ray diffraction patterns.

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要 旨

シリカ担持銀修飾モリブデン触媒による合成ガスとアンモニアからのアセトニトリル合成

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シリカ担持モリブデン系触媒による合成ガスとアンモニアからの直接アセトニトリル合成について触媒調製条件, 助触媒の影響を調べた。

まず, Mo/SiO_2 触媒について調製条件の影響を調べた。触媒は, モリブデン酸アンモニウム水溶液をシリカに含浸し空気焼成後還元して調製した。本反応の主生成物はアセトニトリル, 二酸化炭素 および 炭化水素類であった。空気焼成のみの触媒 A, 空気焼成後水素還元した触媒 B, 空気焼成後アンモニア還元した触媒 C の三つの触媒の反応結果を **Table 1** に示したが, ほとんど違いは認められなかった。この原因を調べるため触媒の反応前後の X 線回折をとり **Fig. 1** に示した。触媒 B は反応前後とも MoO_2 のパターンを示すのに対し, 触媒 A は反応前は MoO_3 , 反応後は MoO_2 のパターンを示した。触媒 A は反応中に還元されて触媒 B と同じく MoO_2 が担持されている形態になるため, 反応結果に変化がないものと理解された。このことは, 触媒 B の活性変化が単純に低下しないことから支持される。

次に, Mo/SiO_2 に対して第二金属成分を添加しその効果を調べた結果を **Table 2** に示す。アルカリ金属, アルカリ土類金属はアセトニトリル生成活性選択性を低下させ好ましくなく, 第 8 族金属もほぼ同様の結果であった。しかし, Ag はアセトニトリル生成活性を上げると同時に選択率も 50% 増大させる効果があることが分かった。Ag の助触媒効果についてはいまだ報告はない。**Fig. 2** に Ag の添加量の影響を示したが,

Ag はほんの少量で効果を現すことが分かる。**Fig. 3** に示した反応温度の影響から, アセトニトリル生成の最適温度は 450–500°C であった。また, 接触時間の影響を示した **Fig. 4** では, ある範囲内で収率と比例関係にあった。

Ag の効果を調べるため, 種々の触媒分析を行った。熱天秤による還元処理での重量変化から Mo/SiO_2 , Mo-Ag/SiO_2 いずれの触媒においても水素還元で Mo は MoO_2 の形となっており, 一方 **Fig. 5** に示した XPS 測定でも表面での Mo の価数に Ag の影響は認められなかった。しかし, **Figs. 6, 7, 8** に示した X 線回折測定から Ag の効果が明らかとなった。**Fig. 6** は空気焼成後の X 線回折図であるが, Ag と Mo は複合酸化物を形成する。**Fig. 7** は水素還元後の回折図であり, Ag がいないときには MoO_2 , Ag が存在すると Mo 金属と Ag 金属の回折ピークが認められる。しかし他の情報から Ag が存在する場合でも Mo は MoO_2 の形で存在していると考えられ, おそらく Ag の存在は MoO_2 を無定形か高分散状態にする働きをしているものと推定された。Mo 金属が反応活性種となっていないことは **Fig. 8** の反応後の回折図でそのピークが完全に消失していることから確かめられた。

触媒活性の経時変化を **Fig. 9** に示すが, 活性は時間とともに低下している。X 線回折測定から MoO_2 の結晶成長が触媒劣化と関係があることが示唆されるが, 表面への炭素質あるいは有機物の沈着もひとつの原因になっているものと考えられた。

Keywords

Acetonitrile, Ammonia, Molybdenum catalyst, Silver, Syngas, X-ray diffraction