A Study on the Sulfur-Resistant Catalysts for Water Gas Shift Reaction
III. Modification of Mo/γ-Al₂O₃ Catalyst with Iron Group Metals

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Mo/γ-Al₂O₃ catalysts modified with Fe, Co, and Ni were prepared by impregnation method and catalytic activity for water gas shift reaction was examined. The optimum amount of Mo loaded for the reaction was 10 wt% MoO₃ to γ-Al₂O₃. The catalytic activity of MoO₃/γ-Al₂O₃ was increased by modifying with Fe, Co, and Ni in the order of Co ≈ Ni > Fe. The optimum amounts of Co and Ni added were 3 wt% based on CoO and NiO to 10 wt% MoO₃/γ-Al₂O₃, respectively. The TPR (temperature-programmed reduction) analysis revealed that the addition of Co and Ni enhanced the reducibility of the catalysts. The results of both catalytic activity and TPR experiments strongly suggest that the redox property of the catalyst is an important factor in water gas shift reaction on the sulfided Mo catalysts, which could be an evidence of oxy-sulfide redox mechanism.

Introduction

Many researchers have studied the development of alternative carbon sources to overcome the shortage of carbon sources. Those activities were concentrated on the utilization of coal as a novel carbon source. One of the main usage of coal is coal gasification to produce syngas. however, the quality of syngas produced from coal gasification is not good for methane synthesis because the ratio of CO/H₂ is over 1.[1] Therefore, water gas shift reaction process is needed for the conversion of excess carbon monoxide to hydrogen.[2,3] In a commercial process, a two stage water gas shift process which consists in Fe-Cr catalyst and successive Cu-Zn catalyst. However, these catalysts are not applicable for the water gas shift reaction of syngas derived from coal because they are very sensitive to impurities such as sulfur and chlorine compounds.[4]

In 1912, Bosch and Wild developed Fe-Cr catalyst for water gas shift reaction and it was adopted in ammonia synthesis process in 1915.[2] Water gas shift reaction has been widely used in ammonia synthesis process to produce hydrogen from carbon monoxide and to protect ammonia synthesis catalyst from deactivation by carbon monoxide.[3] The reaction equation and equilibrium suggested by Moe are as follows.[5]

$$H_2O(g) + CO(g) = H_2(g) + CO_2(g) \ (\Delta H = -41 \text{ kJ/mol})$$
$$K_p = \exp[4577.8/T - 4.33] \qquad (\text{T: Kelvin})$$
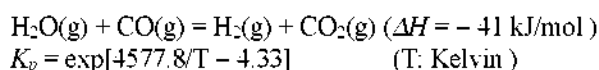
This reaction is exothermal and the lower the reaction temperature, the better the conversion. Fe-Cr catalyst, a high temperature catalyst, is operated in the temperature range of 320-450 °C. It consists of the solid solution of Fe₂O₃ and Cr₂O₃ and is permanently deactivated by chlorine and sulfur (over 50 ppm).[4] Cu-Zn catalyst, a low temperature catalyst.

is operated in the temperature range of 200-250 °C.[6,7] It is permanently deactivated by very small amounts of chlorine and sulfur. To overcome the deactivation by impurity, screening of catalysts for water gas shift reaction with robust catalytic activity has been carried out.[8,9] Some researchers reported that sulfided forms of CoMo and NiMo supported on γ-Al₂O₃ showed good catalytic activity in the presence of sulfur.[3,10-12] These catalysts are widely used in the field of hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, hydrodemetallization, and Fisher-Tropsch reaction.

Metal oxides that are supported on stable supports such as γ-Al₂O₃ and SiO₂ are widely used as catalysts for various chemical reactions. Supported metal oxides show different reduction behavior from unsupported ones. The difference of reduction property plays an important role in catalysis. TPR (temperature-programmed reduction) is a widely used analytical technique to investigate the reduction behavior of metal oxides because characterization of catalysts by TPR is easy and time saving.[13-15]

In the present study, we performed mainly TPR analysis for various γ-alumina-supported MoO₃ samples modified with Co and Ni. The TPR results were compared with the catalytic activity for water gas shift reaction. We will report, in this paper, the relationship between the reduction properties and the activities of the γ-alumina-supported molybdenum oxide modified with Co and Ni for water gas shift reaction.

Experimental Section

Preparation of Catalysts. A series of yM, xCyM, xNyM, and xFyM samples were prepared by impregnation of γ-Al₂O₃ (Catalysis Society of Japan, JRC-ALO-2) with an aqueous solution of (NH₄)₆Mo₇O₂₄ · 4H₂O (Oriental, EP). The desired amount of Co(NO₃)₂ · 6H₂O (Shinyo, EP), Ni(NO₃)₂ · 6H₂O (Shimaku, EP), and Fe(NO₃)₃ · 9H₂O (Kanto, EP) were added to the above solution as a metal precursor. The value y is the loading amount of Mo in wt% of

MoO₃ to γ-Al₂O₃ and x is the loading amount of the Co, Ni, and Fe in wt% of CoO, NiO, and Fe₂O₃ to γ-Al₂O₃, respectively. Water was removed by a rotary vacuum evaporator at 50 °C. Thereafter the samples were dried in air at 105 °C for 2 hours, and finally calcined at 500 °C for 5 hours.

Catalytic Activity Test. Sulfidation was performed before water gas shift reaction experiment because the calcined catalysts are in oxide form. The calcined catalyst was loaded on 100-mesh quartz frit (10 mm of diameter) located inside a quartz tube. The amount of the catalyst was 300 mg. Reactor temperature was raised to 450 °C under N₂ flow and 50% H₂/H₂S (20 mL/min) flow was introduced for sulfidation for 1 hour. After sulfidation the reactor temperature was dropped to 400 °C under N₂ flow to remove residual H₂S for 30 min. Water was introduced by a syringe pump (Keun-A Co., KASP005/150MT). The inlet and outlet of the reactor was kept over 120 °C to prevent the condensation of water. Reaction temperature was 400 °C and flow rates of water, CO. and N₂ were 7, 7, and 14 mL/min. respectively. Products were analyzed by on-line GC (Packard Co.) equipped with TCD. Charcoal packed column (60-80 mesh, 1/8 in. × 2 m) was used for the analysis of the products. Catalytic activity was calculated with a following equation.

$$\text{CO conversion (\%)} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100$$

TPR Analysis. TPR apparatus was used to investigate the surface structure and the oxidation state of samples. The schematic diagram of TPR apparatus was shown in a previous paper.[16] For this experiment, 40 mg of a sample was placed on a sintered quartz frit (10 mm of diameter) located inside a quartz tube. For the reduction of the sample, a H₂ (1.5 mL/min)/N₂ (28.5 mL/min) flow gas was used and heating rate was 10 °C/min.

BET Surface Area Analysis. Nitrogen (99.99%) and helium (99.99%) were used as an adsorbate and an inert gas, respectively in a commercial BET apparatus (Quantasorb M).

Results and Discussion

Mo Catalyst: A series of samples with different Mo loading were prepared. Their BET specific surface areas and the surface areas calibrated to the amount of a support are shown in Table 1. The surface area decreased with the increase of Mo loading, which suggested that the pore mouth of the support was plugged by the formation of large MoO₃

Table 1. BET surface areas and calibrated BET surface areas of various xM catalysts

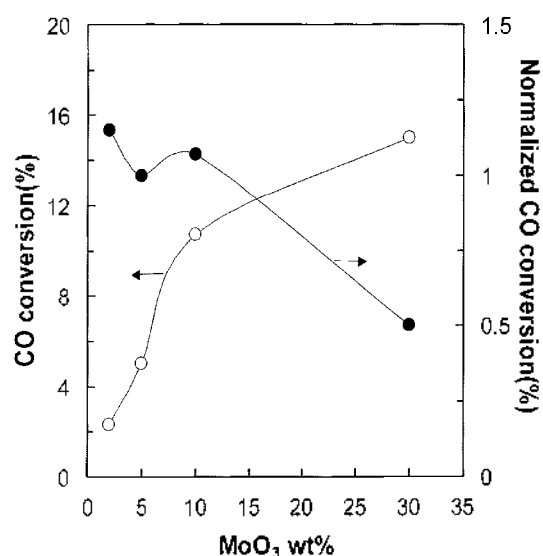| Catalyst	BET S. A. (m²/g)	Calibrated BET S. A. (m²/g)
0M	193	193
2M	190	193
5M	189	199
10M	162	179
30M	136	177

Figure 1. CO conversion of (a) 2M, (b) 5M, (c) 10M, and (d) 30M.

particle. Figure 1 shows the catalytic activities of yM catalysts for water gas shift reaction. The CO conversion increased with the increase of Mo loading. There are two possible ways of activity enhancement. One is the increase of the amount of active sites, and the other is transformation of active sites to more active ones. CO conversion enhancement up to 10M was attributed to the increment of the amount of active sites. Therefore, 2M. 5M. and 10M showed similar normalized CO conversion. Normalized CO conversion is CO conversion divided by corresponding wt% of Mo. Theoretically. monolayer of MoO₃ covers the support in the case of 10 wt% loading of MoO₃. which was confirmed by Goldwasser *et al.* with CO adsorption. CO₂ adsorption. and ion scattering spectroscopy.[17] However, there is still the increase of CO conversion in the case above 10M. This suggested that the properties of the supported MoO₃ were changed with the increase of MoO₃ loading. We deduced that the catalytic activity for water gas shift reaction was controlled by the properties of active sites as well as the number of active sites for γ-alumina supported MoO₃. The effective loading amount of MoO₃ was 10 wt% considering turnover frequency.

Figure 2 shows TPR spectra of the samples with different Mo loading. Two peaks were observed in the region of 500-670 °C (low temperature peak) and above 900 °C (high temperature peak). respectively. Figure 2 revealed that the reduction of Mo oxide became easier with the increase of Mo loading. A peak was observed at about 700 °C with a different peak shape for pure γ-alumina suggesting the removal of surface hydroxyl group by hydrogen.[16] We supposed a certain repulsive lateral interaction which was enhanced with the increase of the oxide loading up to monolayer coverage resulting in easier reduction if we assumed the same particle size in this region of coverage. And we already suggested that the low temperature peak was related to polymeric octahedral molybdate located on top of oxide
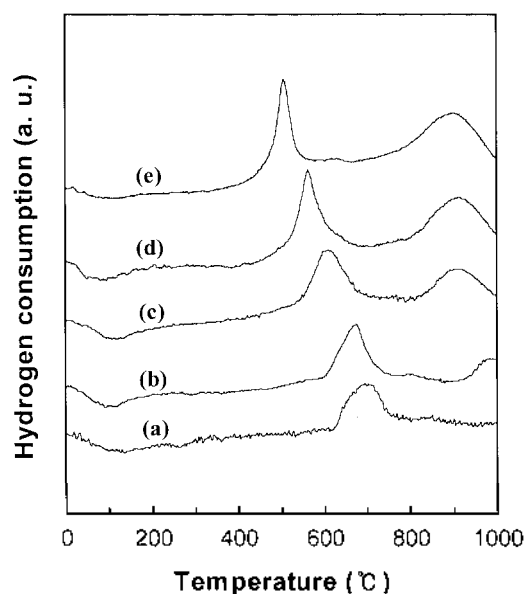
Figure 2. TPR profiles of (a) 0M, (b) 2M, (c) 5M, (d) 10M, and (e) 30M.

multilayer.[16] Peak width of the low temperature peak increased with the increase of MoO₃ loading which supposed that the interaction between the support and molybdate on top of the oxide multilayer became weaker. Ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] is widely used as a molybdenum precursor. Mo is octahedrally coordinated (Mo[O]) in polymolybdate compounds which is easily transformed to tetrahedral coordination (Mo[T]) by a drying process.[18] Both Mo[O] and Mo[T] exist after calcination and the amount of Mo[O] increases by increasing Mo loading.[19]

Figure 3 shows the oxy-sulfide redox mechanism suggested by Hou *et al.*[20] They suggested that the active site was oxy-sulfide form of Mo^{5-} that was generated by the substitution of one oxygen atom for sulfur atom (A and B). This oxy-sulfide form of Mo^{5+} was reduced to Mo^{4+} with a
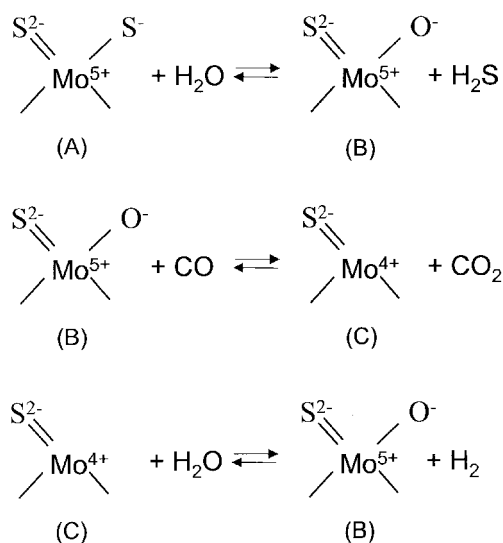

Figure 3. Schematic diagram of oxy-sulfide redox mechanism.
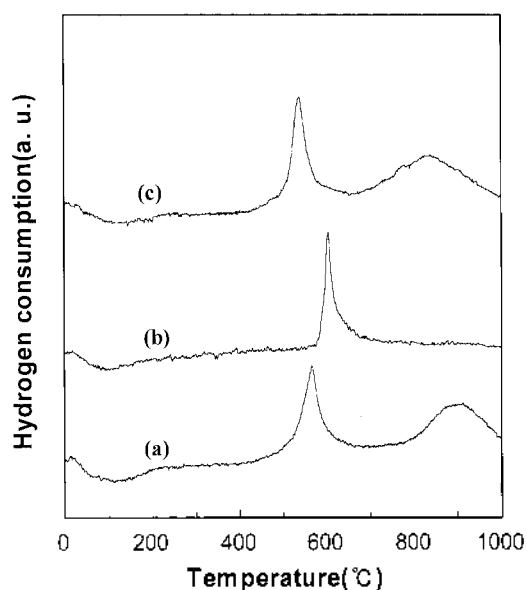

Figure 4. TPR profiles of (a) 10M, (b) 3C, and (b) 3C10M.

vacancy by the reaction of CO and coordinated oxygen to produce CO_2 (B and C). Reduced Mo^{4+} was easily reoxidized to Mo^{5-} by H_2O and H_2 was produced (C and B). Eventually, the oxy-sulfide form of Mo^{5-} worked as a catalyst and the water gas shift reaction happened. Comparing TPR result and CO conversion data of 10M and 30M both of which had similar amounts of exposed Mo atoms, higher CO conversion of 30M was attributed to better reducibility, which was well correlated with the oxy-sulfide redox mechanism.

(Fe, Co, Ni)-Mo Catalysts: The addition of iron group metals such as Fe, Co. and Ni are known to improve the catalytic activity of molybdenum catalyst. Figure 4 shows TPR spectra of 3C. 10M. and 3C10M. The addition of Co made both the low temperature peak and the high temperature peak shift to lower temperature. The addition of Co gave enhanced reducibility to 10M and the characteristic reduction peak of cobalt oxide disappeared which suggested that the added cobalt became homogeneous oxide with molybdenum. The high temperature peak became broader by the addition of Co which meant that the surface oxide of 3C10M was more heterogeneous than that of 10M. Arnoldy *et al.* reported similar TPR behavior of CoMo catalysts.[21] Nag *et al.* have suggested that the low temperature peak and the high temperature peak were related to CoO and MoO₃, respectively,[22] which is thought to be a wrong understanding. however. there is a consensus that the addition of CoO and NiO enhanced the reducibility of MoO₃.[21,22]

Figure 5 shows the effect of Fe, Co. and Ni. Activity order of water gas shift gas reaction was Ni (7.2%) > Co (4.2%) >> Fe (1.1%) for single element. Activity order of combined catalysts was CoMo (23.9%) ≈ NiMo (23.6%) > FeMo (11.2 %). The activity of 10M was 10.7% of CO conversion. Therefore, the addition of Fe showed no synergistic effect. while the addition of Co gave a dramatic synergistic effect on water gas shift reaction. To check the effect of loading
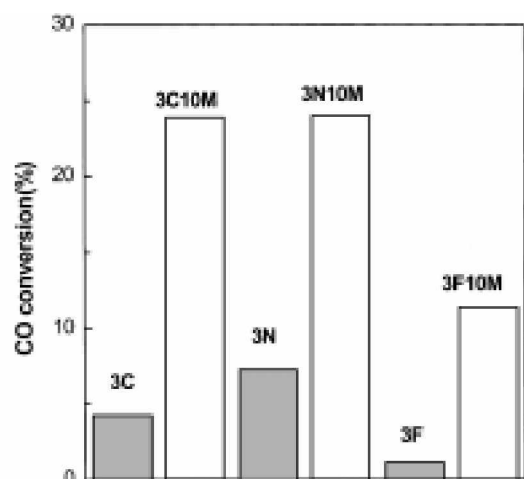
Figure 5. CO conversion of various catalysts.

Figure 7. TPR-S profiles of 3C10M, 3N10M, and 3F10M.

sequence, three different 3C10M catalysts were prepared, those were Co pre-impregnated, Mo pre-impregnated, and co-impregnated. It was observed that they showed almost the same activity for water gas shift reaction. It was understood that the difference of surface oxides formed by different loading sequence was cancelled by high temperature calcination. In other words, the sequence of impregnation was not important in this catalytic system. Therefore, we adopted co-impregnation method for the convenience of catalyst preparation.

Figure 6 shows TPR patterns of 3C10M, 3N10M, and 3F10M. They showed similar TPR patterns. 3N10M showed broader reduction peak which meant the catalyst was not so much homogeneous and 3F10M showed the highest reduction temperature even if the difference is small. To identify the different synergistic effect of FeMo catalyst, TPR analysis of sulfided catalyst (TPR-S) was carried out. TPR-S patterns of catalysts are shown in Figure 7. The TPR-S peak of
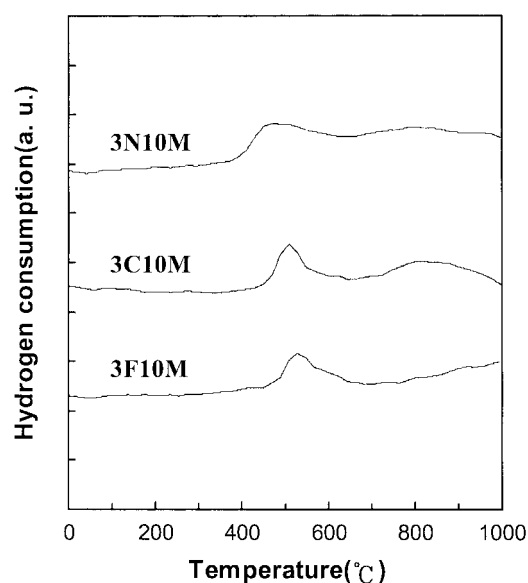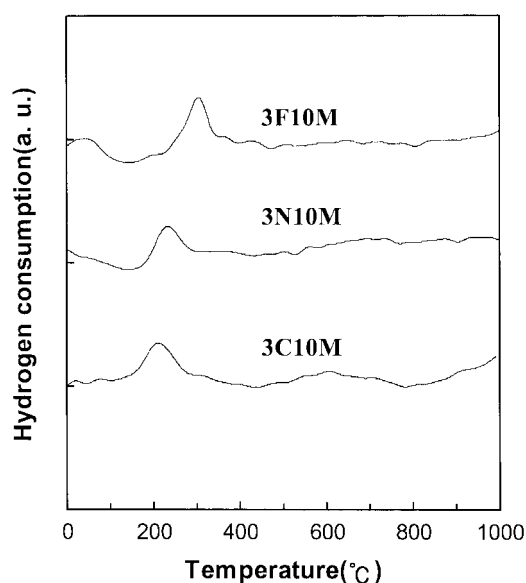
FeMo (311 °C) was rather higher than those of CoMo (220 °C) and NiMo (240 °C). CoMo and NiMo showed similar TPR-S peak. We suggested that the difference of synergistic effect was attributed to the different reducibility of the catalysts.

Effects of Ni and Co concentration: To understand the effect of Co and Ni and to find out the optimum loading amount of Co and Ni, various xC10M and xN10M catalysts were prepared. Figure 8 shows CO conversion of the catalysts as a function of CoO and NiO loading. The maximum CO conversion was achieved in the region of 3-5 wt% of CoO and NiO, respectively. Co and Ni showed similar catalytic behavior while CoO showed slightly higher conversion in the case of 10 wt% loading amount. This implied that the effect of CoO and NiO became different when loading
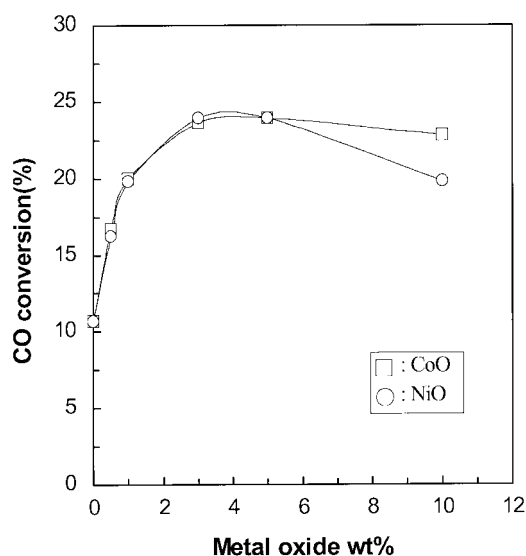

Figure 6. TPR profiles of 3C10M, 3N10M, and 3F10M.

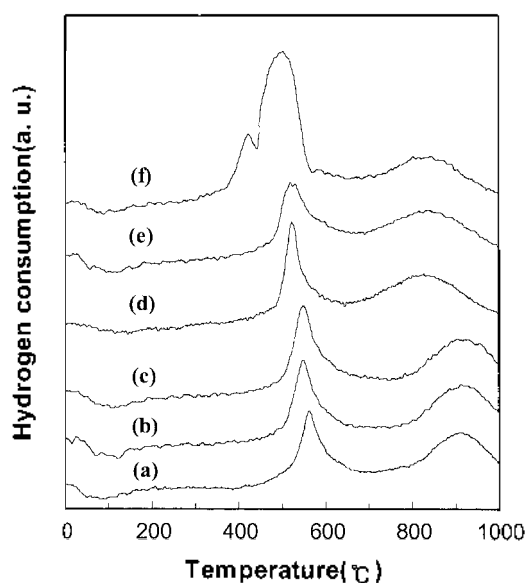**Figure 8.** Effect of CoO and NiO loading on CO conversion over 10M catalyst.

Figure 9. TPR profiles of (a) 10M, (b) 0.5C10M, (c) 1C10M, (d) 3C10M, (e) 10C10M, and (f) 50C10M.

amount of CoO and NiO was over 10 wt%. The similar tendency is observed in other catalytic reactions such as hydrodesulfurization and hydrodenitrogenation. 3C and 3N were also prepared to check the catalytic activity of γ-alumina supported CoO and NiO. They showed different CO conversion (3C : 4%, 3N : 7%). In summary, NiO and CoO showed different catalytic activity. However, they formed mixed oxide with MoO₃ and gave almost the same effect when small amount was added in spite of their intrinsic differences in oxide state. XRD analysis of these compounds did not show any significant metal oxide peak due to a small amount of metal oxide.
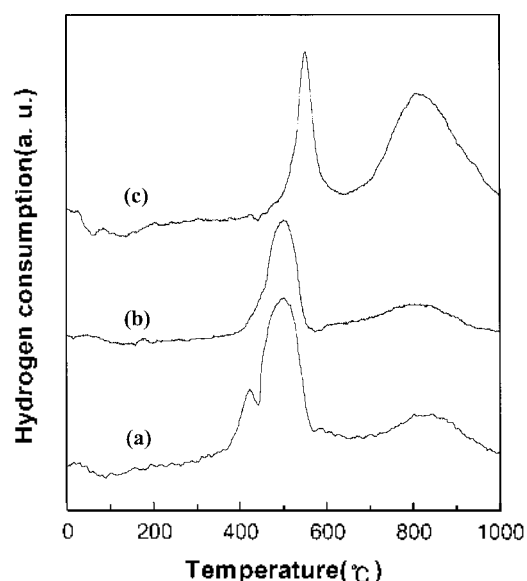
Figure 9 shows TPR spectra of xC10M catalysts. Low

temperature peaks were shifted to lower temperature as the amount of CoO increased. This tendency continued up to 3 wt% CoO. The reduction peak temperature did not change in the case above 3 wt% CoO, however, the low temperature peak became broader with the increase of CoO amount. A new TPR peak appeared beside the low temperature peak when an excess of CoO (over 50 wt%) was added. The new peak was assumed to be the reduction peak of CoO, in isolated form.[23] having similar properties to bulk CoO. Mcnicol *et al.* reported that the reduction temperature of bulk CoO was 400 °C which well matched with our results.[24] This characteristic peak of CoO disappeared with the elevation of calcination temperature which was attributed to the formation of CoMoO₄ and CoAl₂O₄ by increased thermal energy as shown in Figure 10. The shift of the low temperature peak to higher temperature was assumed to be related to the surface change of the support by the formation of CoAl₂O₄. Massoth reported that the penetration of Co into subsurface of alumina changed the surface charge to neutral by the substitution of aluminum or combination with surface oxygen.[19] We deduced that CoO formed homogeneous oxide with MoO₃ and it was more readily to be reduced than pure MoO₃ when a small amount was added and the mixed oxide of CoO and MoO₃ became more heterogeneous with the increase of CoO loading. In the case of the high temperature peak. the peak shifted to lower temperature as the loading amount of CoO increased. However, the peak area was almost constant because the state of Co remained metallic and that of Mo was MoO₂ after undergoing low temperature reduction. Ratnasamy *et al.* suggested three states of Mo species. One was Mo[T] (Al₂(MoO₄)₃). very difficult to reduce. another was bulk like MoO₃, easy to reduce, and the third was Mo[O]. moderate to reduce. They reported that the reducibility of Mo[O] increased by the addition of Co.[25]

Figure 11 shows TPR spectra of xN10M catalysts. Reduc-

Figure 10. TPR profiles of 50C10M calcined at (a) 500 °C, (b) 650 °C, and (c) 800 °C.
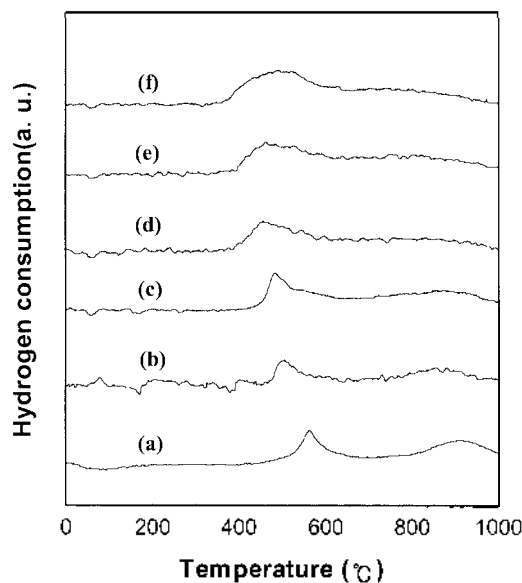

Figure 11. TPR profiles of (a) 10M, (b) 0.5N10M, (c) 1N10M, (d) 3N10M, (e) 5N10M, and (f) 10N10M.

tion peak temperature was shifted to lower temperature as the loading of NiO increased. The shift of peak temperature was not observed in the case above 3 wt% NiO addition. In the case of xC10M, the low temperature peak was very sharp. however. xN10M showed low temperature and high temperature peaks both of which were broad. From these results, we suggested that the effect of CoO and NiO addition was the enhancement of reducibility. TPR spectrum of 10N10M was broader and the peak was shifted to higher temperature comparing with 10C10M. Therefore, the lower catalytic activity of 10N10M than 10C10M was thought to be due to the difference of their reduction property.

Conclusions

The optimum amount of Mo loaded for the reaction was 10 wt% MoO_3 to γ-Al_2O_3. The catalytic activity of MoO_3/γ-Al_2O_3 was increased by modifying with Fe, Co, and Ni in the order of Co ≈ Ni > Fe. The optimum amounts of Co and Ni added were 3 wt% based on CoO and NiO to 10 wt% MoO_3/γ-Al_2O_3, respectively. The TPR analysis revealed that the addition of Co and Ni enhanced the reducibility of the catalysts. The results of both catalytic activity and TPR experiments strongly suggest that the redox property of the catalyst is an important factor in water gas shift reaction on the sulfided Mo catalysts, which could be an evidence of oxy-sulfide redox mechanism.

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