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# CoMo bimetallic nitride catalysts for thiophene HDS

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CoMo bimetallic nitride catalysts were prepared by temperature-programmed reduction of CoMo oxides with flowing ammonia, and the effects of cobalt addition on the thiophene hydrodesulfurization (HDS) reaction were investigated. $MoO_3$ transformed into $Mo_2N$, while cobalt oxide was just reduced to Co metal rather than Co nitride. When Co was added to Mo, the surface area decreased significantly but the new bimetallic nitride phase of $Co_3Mo_3N$ was produced. The addition of Co could improve the HDS conversion, and the high specific activity of the bimetallic nitride catalyst was believed to be related with the new $Co_3Mo_3N$ phase.

**Keywords:** thiophene HDS, temperature-programmed reduction with $NH_3$, CoMo, bimetallic nitride, Rietveld analysis, $Co_3Mo_3N$

## 1. Introduction

Among the efforts to develop more effective hydrotreating catalysts, several studies reported that high surface area molybdenum nitride ($Mo_2N$) showed high hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities comparable to those of commercial alumina-supported catalysts [1–4]. Especially, $Mo_2N$ was a useful catalyst for HDS and HDN because it was reactive toward direct removal of sulfur and nitrogen with less consumption of hydrogen [4,5]. Syntheses of other bimetallic nitrides such as $CuWN_2$, $FeWN_2$, $Ni_3Mo_3N$ and V–Mo–O–N have been reported as ways of making new materials [6–9].

The cobalt species in the CoMo bimetallic sulfide catalysts were well known to show synergistic effects on the catalytic activity [10,11]. Although the electronic properties, the crystal structure and porous particle morphology of $Mo_2N$ differ greatly from those of layered $MoS_2$, it was also expected that addition of Co should affect the catalytic properties of $Mo_2N$ in whatever ways it can do. However, few studies have been carried out in this regard about nitriding of CoMo oxide.

In this study, CoMo bimetallic nitride catalysts were prepared through temperature-programmed reduction of the corresponding oxides with flowing $NH_3$ and the effects of Co addition on the thiophene HDS activity were investigated. X-ray diffraction, elemental analysis and scanning electron microscopy were also carried out to obtain better insights into the analysis of the CoMo bimetallic nitrides.

## 2. Experimental

### 2.1. Preparation of catalysts

CoMo oxide samples with various relative Co atomic ratios were prepared by evaporating aqueous solutions of $Co(NO_3)_2 \cdot H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ followed by calcination in air at 500°C for 4 h. Surface areas of the prepared CoMo oxide samples are shown in table 1. Nitriding of the CoMo oxides was performed in a quartz reactor following the procedure of Thompson et al. [4]. One gram of CoMo oxide was nitrided by temperature-programmed reduction with ammonia. The reduction temperature was rapidly increased from room temperature to 350°C over 30 min, then increased to 450°C over 150 min, increased from 450 to 700°C over 75 min, and finally held for 60 min at 700°C. The prepared CoMo nitrides were passivated by exposure to 1% $O_2$/He. The ammonia flow rate was fixed to be 160 ml/min.

### 2.2. Thiophene hydrodesulfurization

Thiophene HDS reaction was carried out at 400°C in a stainless steel microreactor operated at 1.5 MPa. The

Table 1
Surface areas of CoMo oxides

| Composition [a] Co/(Co + Mo) | Surface area ($m^2$/g) |
|---|---|
| 0.0 | 4 |
| 0.2 | 12 |
| 0.5 | 16 |
| 0.7 | 16 |
| 1.0 | 4 |

[a] Mol ratio.

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liquid thiophene flow rate was 0.035 ml/min, the mole ratio of hydrogen to thiophene flow rate was 15 and *W*/*F* was 0.57 g-cat min/ml-thiophene. Before starting the reaction, each catalyst was reduced in situ at 400°C for 2 h with flowing $H_2$ at 30 ml/min. Steady state was achieved after about 5 h of run time. Reaction products were analyzed using a gas chromatograph equipped with TCD and the column packed with OV-101.

## 3. Results and discussion

Surface areas of the prepared CoMo nitrides and their catalytic properties for thiophene HDS are summarized in table 2. Mo nitride had a very high surface area. Mo nitride, typically $Mo_2N$, has been known to have high surface area even in excess of 200 $m^2/g$. The reaction between $MoO_3$ and flowing $NH_3$ was termed topotactic because the product Mo nitride had a well-defined crystallographic orientation relative to the $MoO_3$ reactant. A high surface area was achieved when oxygen was removed and replaced with nitrogen without substantial reorganization of the metal lattice [1,2]. But the surface area of bimetallic CoMo nitride decreased significantly with the addition of Co. Eventually, the surface area of the nitrided Co became nearly the same as that of cobalt oxide. This suggests that the topotactic reaction of cobalt oxide with flowing $NH_3$ is difficult to occur to produce porous nitride.

The addition of Co could improve the HDS activity. In spite of the much lower surface area, the HDS conversions of CoMo nitrides, especially CoMo(2 : 8) nitride and CoMo(7 : 3) nitride, were higher than that of Mo nitride, which indicates that cobalt can act as a promoter to enhance the HDS activity of Mo nitride. When the activity was expressed on the basis of surface area, the specific activity showed a maximum at the relative Co atomic ratio of 0.5.

For a better understanding of the bimetallic nitrides, X-ray diffraction and elemental analysis were carried out. The XRD patterns of CoMo oxides and nitrides are shown in figs. 1 and 2, respectively. As shown in fig. 1, mainly $CoMoO_4$ existed at the relative Co atomic ratio of 0.5, and the characteristic XRD pattern of $MoO_3$ plus $CoMoO_4$ appeared for CoMo(2 : 8) oxide, and $CoMoO_4$ plus $Co_3O_4$ for CoMo(7 : 3) oxide [12]. $MoO_3$ transformed into $Mo_2N$ through the reaction with flowing $NH_3$, while $Co_3O_4$ did not form Co nitride but was reduced to Co metal. This agrees well with the aforementioned suggestion that cobalt oxide is difficult to be transformed into nitride phase. However, new XRD peaks were produced after nitriding $CoMoO_4$, the main phase of CoMo(5 : 5) oxide. Even though not conclusive, the high specific HDS activity of CoMo(5: 5) nitride catalyst is believed to be related to this new nitride phase.

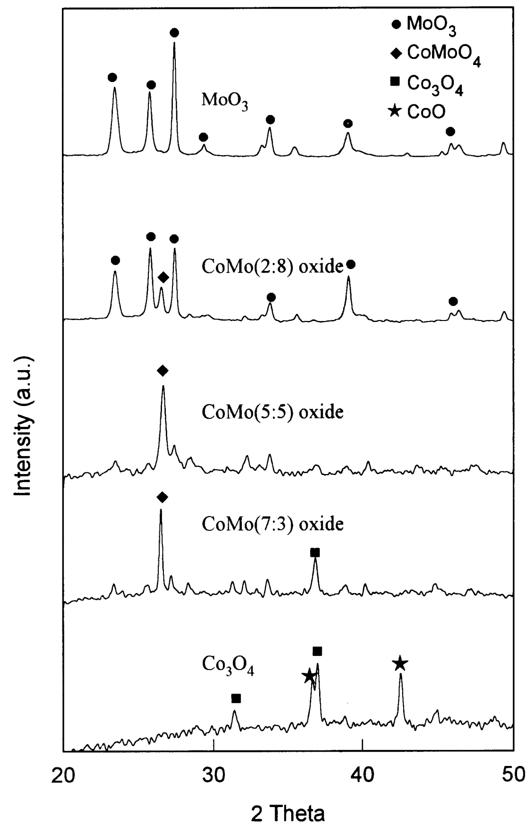

Fig. 1. XRD patterns of CoMo oxides.

Table 2
Surface area and thiophene HDS activity of CoMo nitride

| Composition[a] Co/(Co + Mo) | Surface area ($m^2/g$) | HDS conversion (%) | Specific activity ($\mu mol/(m^2\ min)$) |
|---|---|---|---|
| 0.0 | 115 | 19.5 | 37 |
| 0.2 | 66 | 31.1 | 104 |
| 0.5 | 19 | 13.4 | 155 |
| 0.7 | 41 | 22.8 | 122 |
| 1.0 | 4 | 0.7 | 38 |

[a] Mol ratio.

In table 3 are shown the results of elemental analysis of the prepared CoMo nitride samples. Mo nitride sample had a Mo/N atomic ratio of 1.3, while the extremely high Co/N atomic ratio was obtained after nitriding of $Co_3O_4$. This provides further evidence for the previous results that the topotactic reaction of cobalt oxide with flowing $NH_3$ was difficult to occur. In the case of CoMo(5 : 5) nitride the atomic ratio of both the Co/N and Mo/N appeared to be 2.5, which means that $CoMoO_4$ was changed into N-containing CoMo nitride phase.

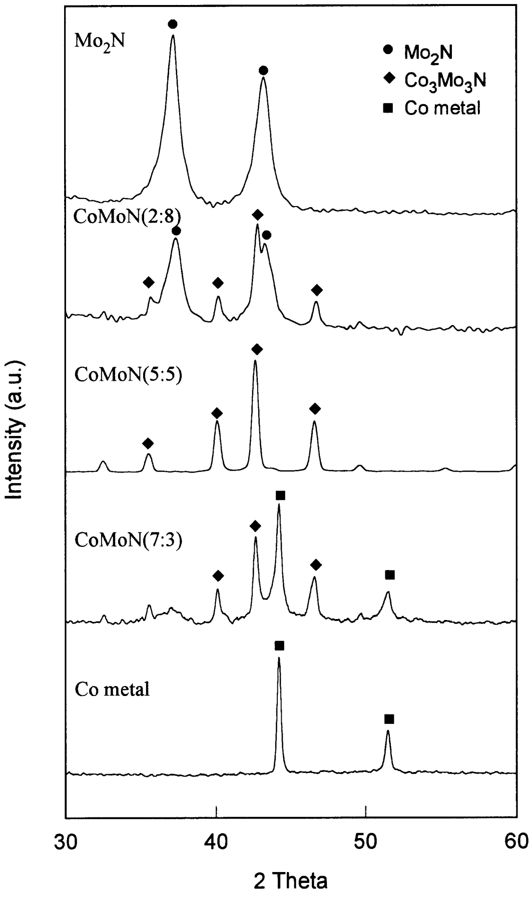

Fig. 2. XRD patterns of CoMo nitrides.

Further studies are needed to elucidate the nature of CoMo(5 : 5) nitride. Bem et al. have reported the XRD pattern of $Fe_3Mo_3N$ using Rietveld analysis [8], and their result really resembles that of the new nitride phase in CoMo(5 : 5) nitride which was $Co_{2.5}Mo_{2.5}N$ from our elemental analysis. Rietveld analysis was done on the assumption that the new XRD peaks of CoMo(5: 5) nitride represent the $Co_3Mo_3N$ phase [13]; the results are shown in fig. 3. The peaks calculated by Rietveld analysis coincided well with the observed XRD pattern. The new nitride phase is then believed to be in the state of $Co_3Mo_3N$. Even if this phase of $Co_3Mo_3N$ remained unchanged even after the HDS reaction at 400°C, some phase changes were observed due to sulfidation in another investigation, the results of which are to be reported elsewhere.

Fig. 4 shows the SEM photographs of CoMo nitrides. In fig. 4A rod-like shapes representing $Mo_2N$ are clearly seen. At the relative Co atomic ratio of 0.2, a needle type morphology newly appeared together with rod-like $Mo_2N$. When compared with XRD results, the needle type phase is believed to be attributable to the new $Co_3Mo_3N$ phase. As the concentration of Co increased the needle type phase agglomerated to form a spherical shape (fig. 4C). In fig. 4D neither rod-like shape nor needle type shape is observable.

## 4. Conclusion

CoMo bimetallic nitride catalysts with different Co/(Co + Mo) ratio were prepared by temperature-programmed reduction of the corresponding CoMo bimetallic oxides with flowing ammonia, and they were employed for the thiophene HDS reaction. The prepared samples were characterized with XRD, elemental analysis and SEM. $MoO_3$ transformed into $Mo_2N$, but $Co_3O_4$ was reduced to Co metal rather than Co nitride. When Co was added to Mo, the surface area decreased significantly, but the new bimetallic nitride phase was produced. From the results of Rietveld analysis, the new

Table 3
Elemental analysis of CoMo nitride catalysts

| Composition[a] Co/(Co + Mo) | Elemental analysis[a] | |
|---|---|---|
| | Mo/N | Co/N |
| 0.0 | 1.3 | – |
| 0.5 | 2.5 | 2.5 |
| 1.0 | – | 59 |

[a] Mol ratio.

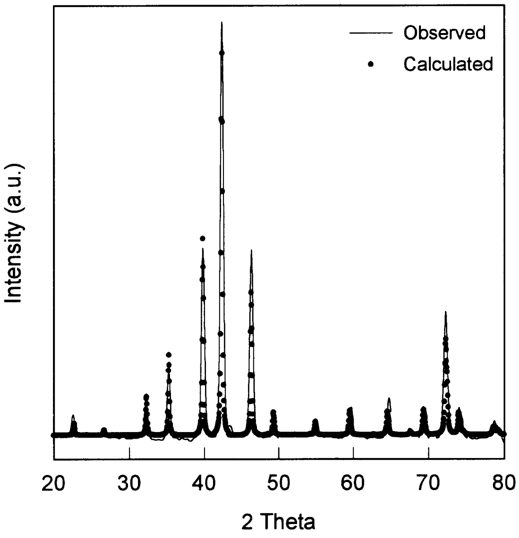

Fig. 3. XRD pattern for $Co_3Mo_3N$ including the Rietveld fit.

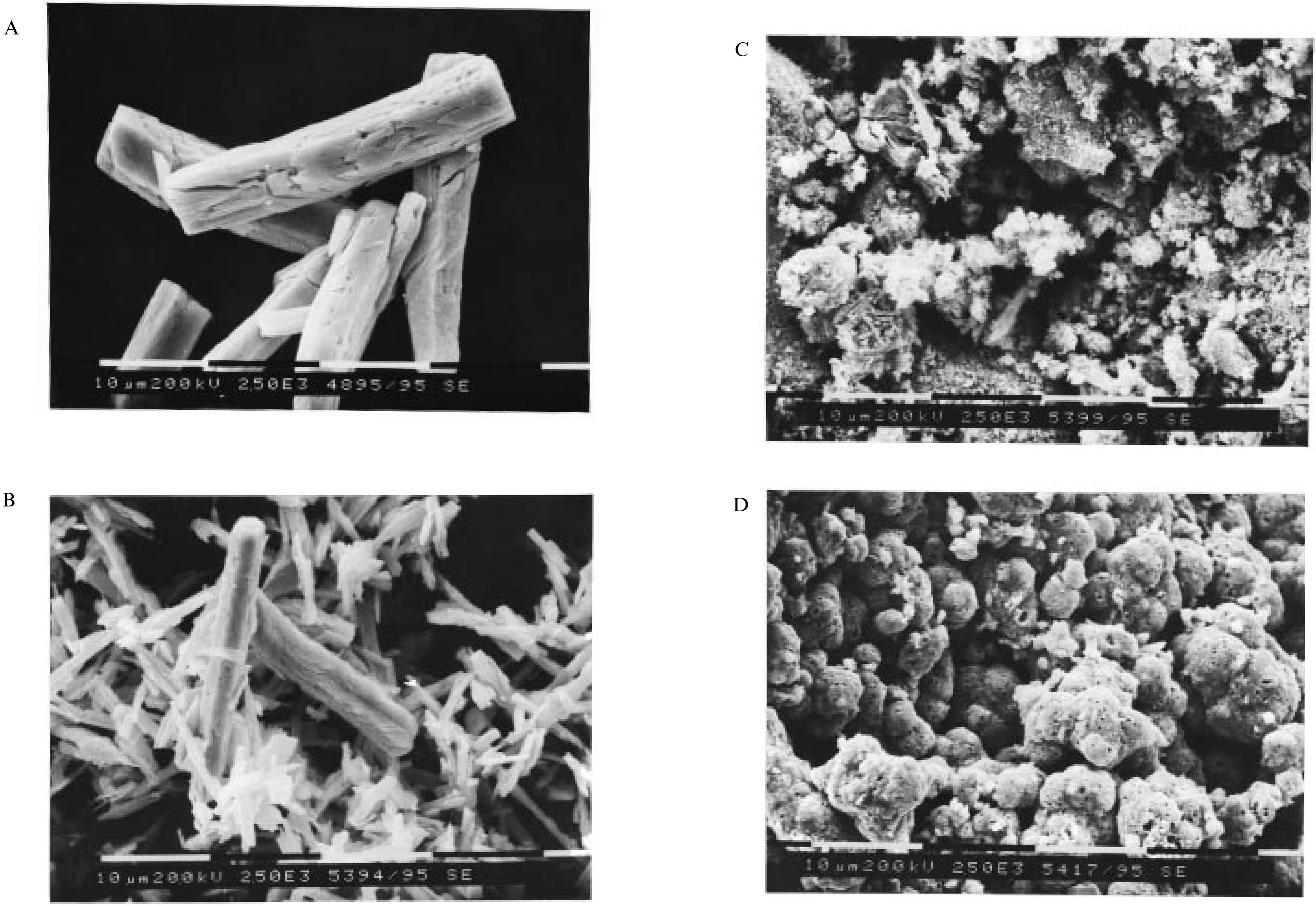

Fig. 4. Representative SEM photographs of CoMo nitride catalysts. (A) CoMo(0: 10) nitride, (B) CoMo(2 : 8) nitride, (C) CoMo(5 : 5) nitride, (D) CoMo(10 : 0) nitride.

bimetallic nitride phase was proposed to be $Co_3Mo_3N$. The addition of Co could improve the HDS conversion, and the specific activity of thiophene HDS was the highest at the relative Co atomic ratio of 0.5. The high specific activity of the catalyst was believed to be related with the new $Co_3Mo_3N$ phase.

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