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Thiophene hydrodesulfurization using unsupported nickel–neodymium bimetal catalysts

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The hydrodesulfurization of thiophene was studied over unsupported nickel–neodymium bimetallic catalysts. The physical and chemical changes of bimetals were observed after calcination and presulfidation, respectively. The activity was increased with addition of neodymium to nickel catalysts and was in good correlation with the surface area of catalysts. Qualitative evidence from XRD and SEM on the role of Nd as a structural promoter were provided.

Keywords: Thiophene hydrodesulfurization (HDS); unsupported catalysts; NdNi (neodymium–nickel) bimetals

1. Introduction

Rare earth intermetallics were reported to be a component of catalysts in various chemical reactions [1–4]. Particularly some patents [5–9] reported that rare earth metals have the effect of significantly reducing the hydrogen pressure required for the hydrodesulfurization (HDS) reaction and enhancing the resistance to coke deposition and hydrogen sulfide. Also it was reported that the metals can improve the activity of hydrodenitrogenation (HDN) and hydrodemetallization (HDM) [9,10].

Mainly due to their ability to store hydrogen or oxygen, various forms of rare earth metals were reported for catalytic reactions; i.e., intermetallic compound [13], hydride [11], oxyhydride [8], oxide [12,14], metal cluster [15] and perovskite [16].

Though rare earth metals were reported to function as active metal, support or promoter, their role has not been well elucidated. Wallace and coworkers [3,17–19] reported the characteristics of rare earth metals for catalytic reactions but they investigated mostly intermetallic compounds. They found that these metals undergo a phase segregation to oxides during calcination and reaction even under

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reducing atmosphere. Recently Gallaher et al. [20] reported that La_2O_3 acts as a support promoter in ethane hydrogenolysis and that its role was well explained as a decoration model.

The aim of the present study is to investigate the catalytic activity of unsupported nickel–neodymium bimetallic species instead of intermetallics and the role of neodymium especially in terms of sintering prevention.

2. Experimental

2.1. PREPARATION OF CATALYSTS

Detailed procedures of precipitation were described elsewhere [8]. Aqueous solutions of nickel and/or neodymium nitrate were introduced drop by drop into a solution of triethylamine (TEA), which was being stirred. Precipitates were decanted out, washed with methanol and subsequently with purified water, dried at 100°C for 24 h and calcined in air at 500°C for 24 h. Five samples with different atomic ratios, Ni : Nd = 1 : 0, 1 : 1/6, 1 : 1/5, 1 : 1/4 and 0 : 1, were prepared.

2.2. PRESULFIDATION AND HYDRODESULFIDATION

0.5–1.0 g of catalyst was loaded in a 1/2″ stainless-steel micro flow reactor. The amount of nickel in each catalyst was fixed to be 5.312×10^{-3} mol. Presulfidation was carried out at 300°C with H_2S/H_2 (10/90) at a flow rate of 60 ml/min. Hydrodesulfurization was carried out at 450°C under atmospheric pressure with a mole ratio of H_2/thiophene = 10 and space time (W/F) = 1155 g-Ni min/mol. The products were analyzed by a gas chromatograph (HP 5890 series II) equipped with a capillary column.

2.3. CHARACTERIZATION

The surface areas of the catalysts were measured by nitrogen adsorption with Autosorb-1 (Quantachrome). The crystallinity, chemical composition and morphology were analyzed by X-ray powder diffraction (Rigaku RAD-3C) and scanning electron micrograph (Hitachi S-2500C).

3. Results and discussion

3.1. CATALYTIC ACTIVITY IN HDS

The catalytic behavior of Ni + Nd bimetals was observed for the hydrodesulfurization of thiophene. It was found that the addition of Nd to Ni catalysts improves their HDS activity. Fig. 1 shows that the Ni + $\frac{1}{5}$Nd catalyst has a higher activity

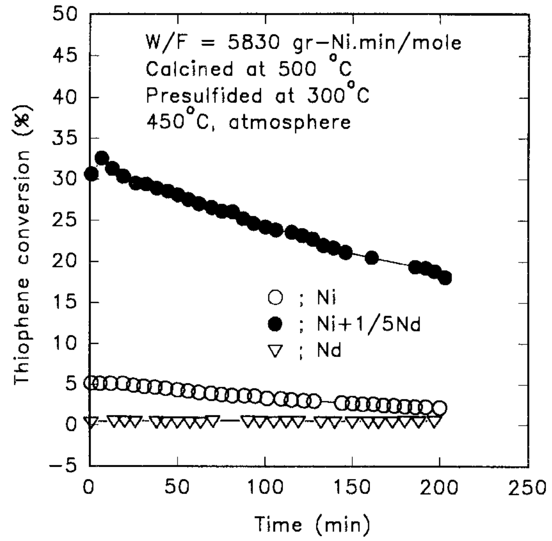

Fig. 1. Catalytic activity of NdNi bimetals in thiophene hydrodesulfurization.

than the Ni or Nd catalyst. The effect of Nd addition was more clearly demonstrated in fig. 2. Pecoraro and Chianelli [21] reported the catalytic activity of NiS_x for liquid phase hydrodesulfurization of debenzothiophene (DBT). By assuming NiS_x to be Ni_3S_2, the catalytic activity is about 2.2×10^{16} molecules of DBT/(g-Ni s). The activity of unsupported Ni catalyst in the present study is about

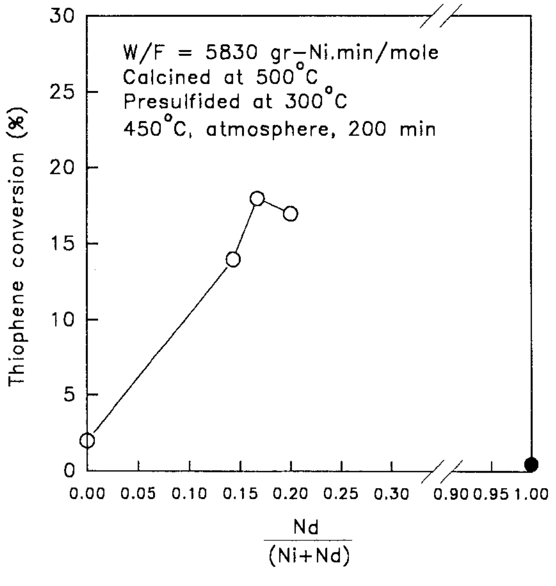

Fig. 2. Effect of Nd addition to Ni (atomic ratio) on the catalytic activity of thiophene hydrodesulfurization ($Ni = 5.312 \times 10^{-3}$ mol).

1.7 × 10^{17} molecules of thiophene/(g-Ni s). The difference in catalytic activity is considered to be mainly due to the difference in the reactants (DBT versus thiophene).

3.2. STATE OF NICKEL AND NEODYMIUM SPECIES FROM XRD

The XRD peaks were obtained for these catalysts in their dried states, calcined states and after presulfidation-HDS reactions as shown in figs. 3, 4 and 5, respectively. In all XRD peaks there was no evidence of an intermetallic compound. It

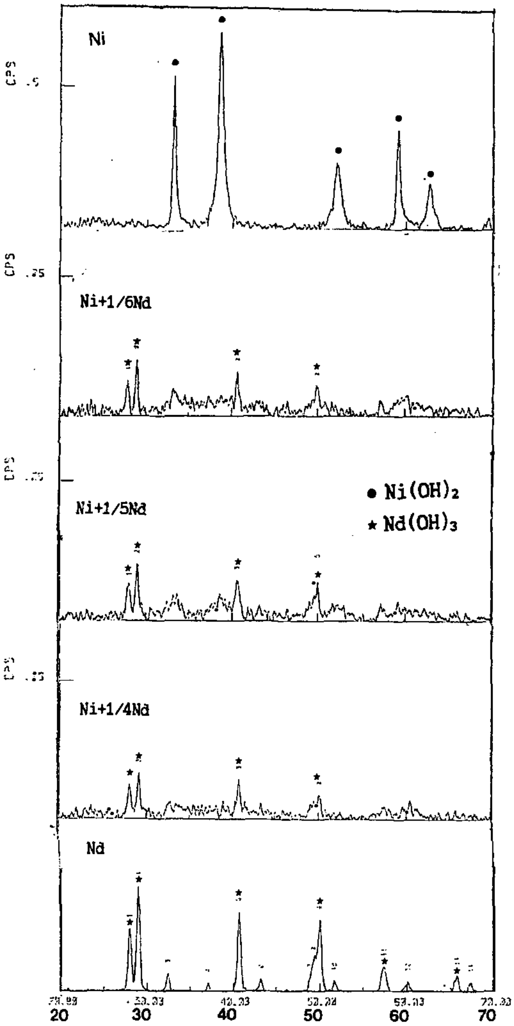

Fig. 3. XRD peaks of the NdNi bimetal catalysts in their dried states.

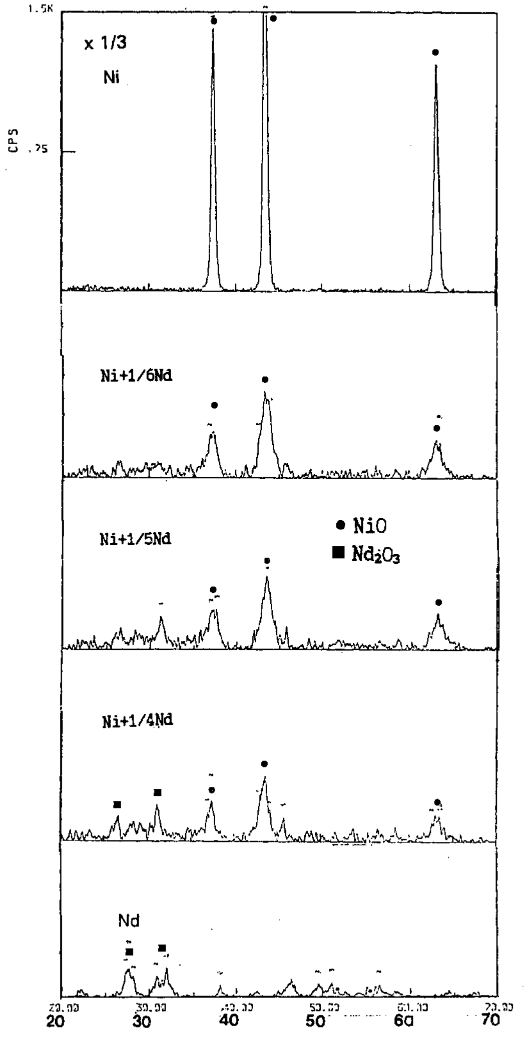

Fig. 4. XRD peaks of the NdNi bimetal catalysts in their calcined states.

can be seen in fig. 3 that the NiNd bimetals exist as hydroxide of each metal in their dried states. The XRD peaks for nickel hydroxide are very well observed in the Ni catalyst, but they all disappeared with addition of Nd as in bimetals like Ni + $\frac{1}{6}$ Nd, Ni + $\frac{1}{5}$ Nd and Ni + $\frac{1}{4}$ Nd. This may suggest that the nickel hydroxides in bimetals are amorphous or their growth was inhibited by addition of Nd. Nickel existed as nickel oxide (NiO) after calcination and as nickel sulfide (Ni_3S_2) after presulfidation as shown in figs. 4 and 5, respectively. Neodymium oxide (Nd_2O_3) was observed only when enough addition (i.e., Ni + $\frac{1}{4}$ Nd) was made (fig. 4). However, neodymium sulfide was not detected in XRD even after presulfidation. Even

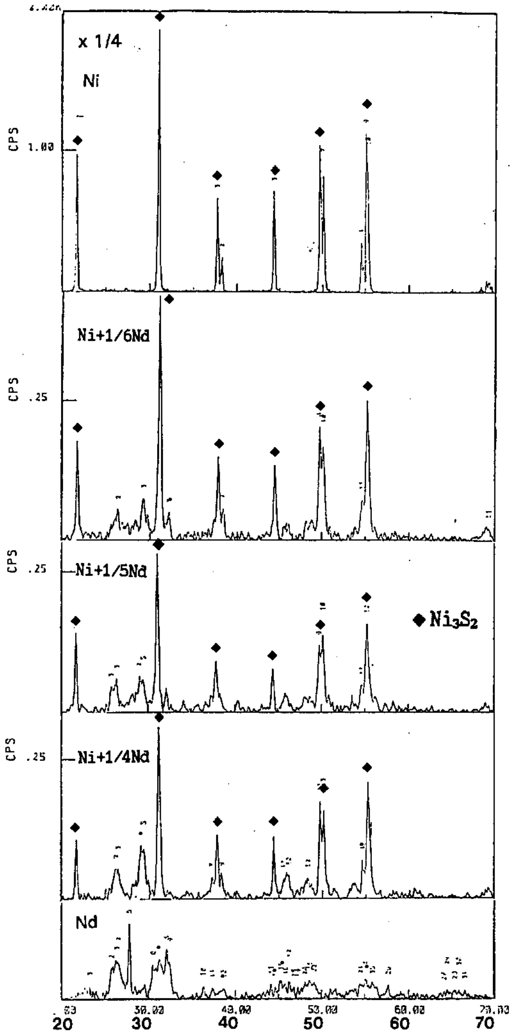

Fig. 5. XRD peaks of the NdNi bimetal catalysts in their states after presulfidation.

though not conclusive, it seems that the neodymium species are decorating the particles of nickel species [20].

3.3. SURFACE AREA AND ACTIVITY

Fig. 6 shows that the surface area (based on unit mass of nickel) decreased due to the calcination and the presulfidation. This may be attributed to sintering. It is believed that neodymium species are very resistant to sintering since their surface area did not change due to calcination or presulfidation. It was found that the catalytic activity for HDS is in good correlation with the surface area (measured after

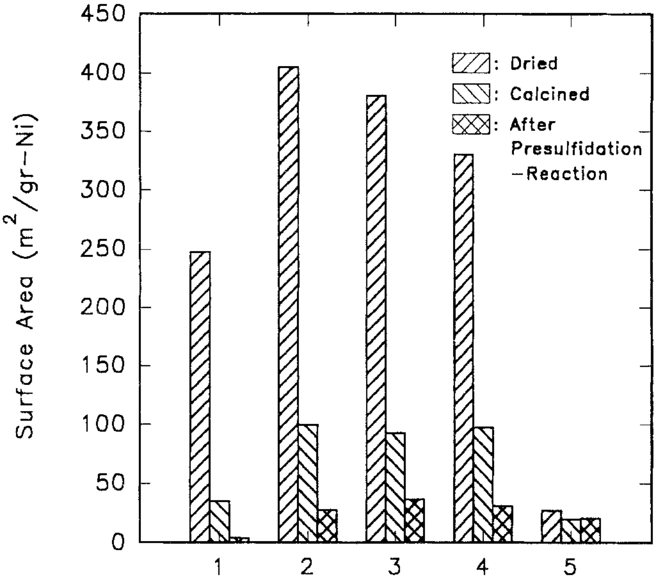

Fig. 6. Changes in surface areas of bimetal catalysts due to calcination and presulfidation. (1: Ni, 2: Ni + $\frac{1}{6}$Nd, d: Ni + $\frac{1}{5}$Nd, 4: Ni + $\frac{1}{4}$Nd, 5: Nd*) {*: surface area (m^2/g-Nd)}.

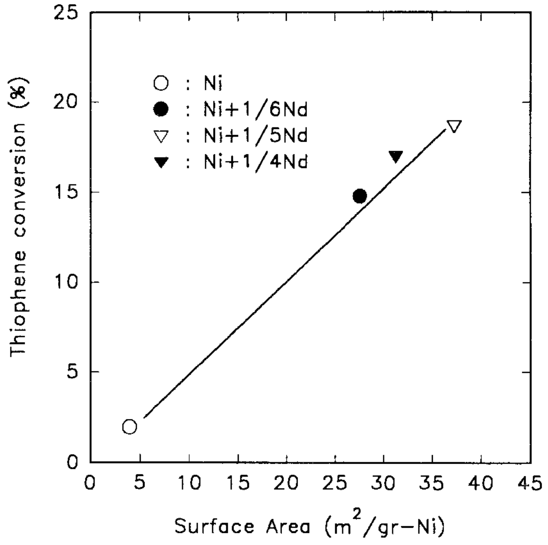

Fig. 7. Correlation between thiophene HDS activity and surface area of NdNi bimetal catalysts.

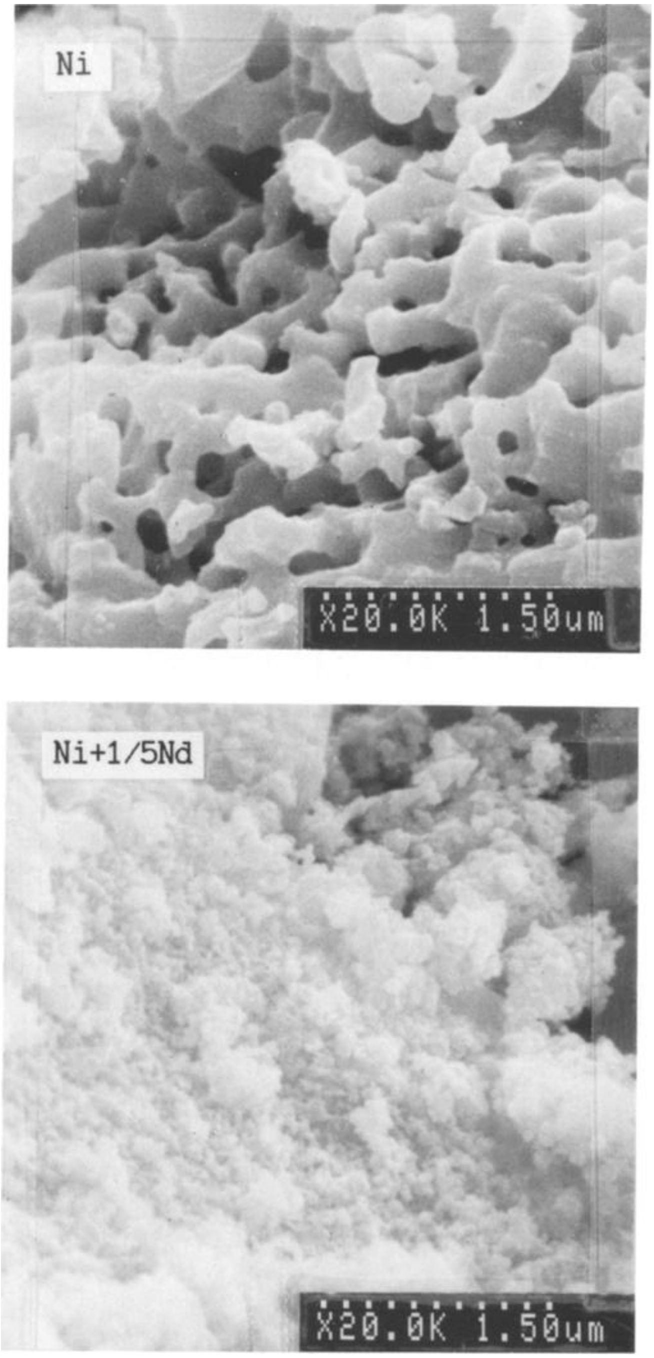

Fig. 8. Scanning electron micrographs of the NdNi bimetal catalysts with different compositions after presulfidation.

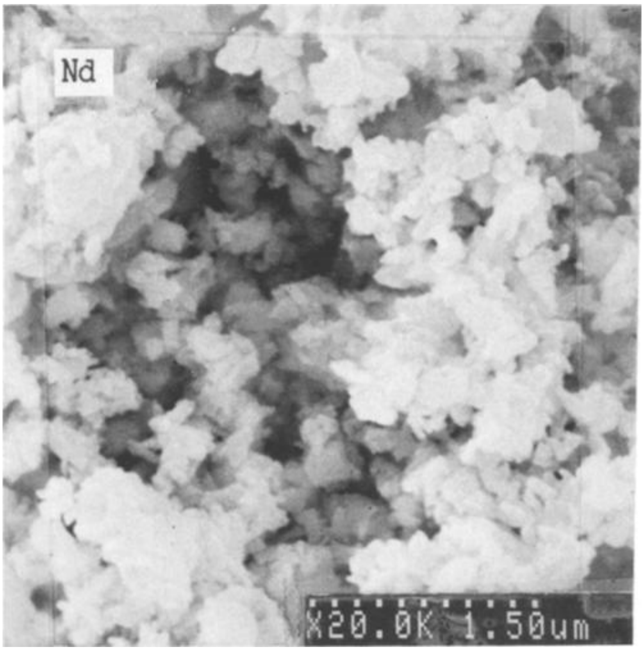

Fig. 8. (continued).

reaction) as shown in fig. 7. This result is rather interesting, since the BET surface area is known not to be correlated with HDS activity especially for MoS_2 catalysts obtained from different preparation methods [22]. In the present study, however, all the catalysts were prepared by coprecipitation, and the Nd species has almost no electronic effect. Furthermore it is suggested that Nd in bimetal catalysts prevents the particles of nickel species from being sintered. Nd plays the role of structural promoter.

The scanning electron micrographs in fig. 8 show the morphology of catalysts after presulfidation. It can be shown that the Ni catalyst has suffered considerable sintering. On the other hand, Nd and $Ni + \frac{1}{5}Nd$ catalysts showed very little sintering.

4. Conclusion

The bimetallic catalysts of NdNi prepared by coprecipitation underwent a drastic change to oxides and sulfides during calcination and presulfidation. When a small amount of Nd was added in Ni, Ni acted as a good HDS catalyst and Nd worked as structural promoter. Thiophene HDS activity of NdNi bimetals was in good correlation with surface area. The role of Nd seems to prevent the sintering of Ni and to keep the high surface area of NdNi bimetal catalyst.

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