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Characteristics of intermetallic $NdNi_5$ as an unsupported catalyst in thiophene hydrodesulfurization

Young-Hwan Moon [a,1] and Son-Ki Ihm

[a] *Samsung Global Environment Research Center, 15th Fl., Samsung Main Bldg., 250, 2-Ga, Taepyung-ro, Chung-gu, Seoul 100-742, Korea*
Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea

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A systematic research is carried out on intermetallic $NdNi_5$ for the hydrodesulfurization (HDS) of thiophene. The effect of calcination and presulfidation of intermetallic $NdNi_5$ on thiophene HDS was examined and property changes of the catalyst during calcination, presulfidation, and reaction were observed by XRD, SEM, and surface area techniques. The intermetallic compound of $NdNi_5$ is disintegrated to fine powder and recrystallized to Nd/Ni oxide and sulfide by calcination, presulfidation, and reaction. A model for the surface area increase of the catalyst during calcination, presulfidation, and reaction was proposed and the role of neodymium was explained.

Keywords: thiophene hydrodesulfurization (HDS); intermetallic compound $NdNi_5$ (nickel/neodymium)

1. Introduction

As the problem of environmental protection is getting serious social concern all over the world, the HDS of petroleum becomes increasingly important. Thus the development of efficient new catalysts is highly desired to prolong the life of catalysts and reduce the severe reaction conditions. In this study the unsupported intermetallic compound $NdNi_5$ was examined as a new HDS catalyst. Rare earth metals have been examined as catalysts since the 1970's [1] and their application in catalytic reactions covers wide areas including methanation [2], hydrogenation [3,4], oxidation [5], catalytic cracking, ammonia synthesis [6] and automative converters [7]. Wallace and coworkers reported several papers on the use of intermetallic compounds in catalytic reactions such as the CO hydrogenation of $LaNi_5$ [8], ammonia synthesis of rare earth/Fe [6], and ethylene hydrogenation of LaNiH [3]. They found that the intermetallic compound catalysts have unique properties such as changing activity, variation in surface area with reaction time, and disintegration of the intermetallic compound. Soga et al. [3] pointed out that the reaction order of hydrogen in ethylene hydrogenation is zero due to the hydrogen storing capability of $LaNi_5$. Some patents [9–11] disclosed the usage of rare earth metals in HDS catalysts and asserted that the conditions of the HDS process can be significantly improved since catalysts containing rare earth metals are little affected by hydrogen partial pressure and sulfur poisoning. Wallace and coworkers [12–16] found that intermetallic compounds undergo chemical and physical changes during reaction. But the role of rare earth metals in catalytic properties is not clear, thus this research is aimed to explain the property changes of intermetallic compounds in catalytic reaction, especially for unsupported $NdNi_5$ intermetallic compound, and the effect of calcination and presulfidation on thiophene HDS activity through observation of SEM, XRD, and surface area.

2. Experimental

Preparation of intermetallic $NdNi_5$. Nd and Ni metal of reagent grade, in which the Ni/Nd atom ratio was 5, were melted in an induction furnace (Tokuda, VG-3L) under argon of 1.7 atmospheric pressure at 1450°C. The melted alloy was poured in a copper tray, cooled, and ground by a ballmill. The powder obtained in this way was washed with acetone and purified water. The intermetallic compound $NdNi_5$ was verified by XRD and used in thiophene HDS as a catalyst.

Pretreatment and reaction. Some amounts of intermetallic $NdNi_5$ powder were calcined at 200, 300, 400, 500, 600 and 700°C in an electro-furnace each for 24 h. 1.5 g (based on the intermetallic compound) of calcined powder was charged in a 1/2″ stainless micro-flow reactor and presulfided using H_2S/H_2 mixture gas, of which the mole ratio is 10/90, with 60 ml/min flow rate at 200, 300, 400, and 500°C each for 4 h. Reaction was carried out under atmospheric pressure at the fixed temperature of 450°C, keeping $H_2/\text{thiophene} = 10$ mole ratio and space time $(W/F) = 5500$ g min/mol. The products were analyzed by a FID gas chromatograph (HP, 5890 series II) equipped with a capillary column.

Instrumental analysis. The surface area of the cat-

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[1] To whom correspondence should be addressed.

alysts was measured by the BET nitrogen adsorption method (Quantachrome, Autosorb-1). The weight change of the catalysts was measured with TG/DTA equipment (Netzsch, STA 409) by calcining in atmosphere up to 1100°C. The crystallinity, chemical composition and morphology were analyzed by X-ray powder diffraction (Rigaku, RAD-3C) using Cu Kα radiation and a scanning electron micrograph (Hitachi, S-2500C).

3. Results and discussion

3.1. Calcination

The prepared massive alloy was verified as the intermetallic compound $NdNi_5$ and the other phase was investigated by XRD measurement. This material was calcined and presulfided and then used as catalyst for thiophene HDS. It was found that calcination and presulfidation affect the HDS activity seriously. In this subsection we describe the calcination effect. HDS activities drastically changed with calcination temperatures and similar results are found in other researches [8,17]. Catalysts calcined below 400°C show low HDS activities, but catalysts calcined above 400°C show relatively high HDS activities. From this phenomenon, the calcination condition is an important factor affecting the thiophene HDS activity of unsupported intermetallic $NdNi_5$. Some previous researchers have also reported the importance of calcination of intermetallic compounds in catalytic reactions [12,13,15,18] but they did not explain the reason sufficiently.

It seems that the surface of catalysts calcined above 400°C is very heterogeneous structurally and energetically in initial reaction time because of micro-cracks or defects due to precipitation (recrystallization) and disintegration of intermetallic $NdNi_5$ during high temperature calcination. The surface heterogeneity reduces by sintering during reaction in reducing atmosphere. Fig. 1 shows the HDS activities obtained after approximately 200 min of reaction for catalysts calcined at different temperatures. The highest HDS activity was obtained after calcination at 400°C and relative high HDS activities were obtained over catalysts calcined above 400°C. Thus it seems there is an optimum calcination temperature in obtaining the high HDS activity. Fig. 2 shows the surface area variation of catalysts which were calcined at various temperatures after calcination, after presulfidation and after reaction. The surface area after calcination is nearly constant but the surface area is slightly increased after presulfidation and remarkably increased after reaction. The mechanism of the surface increase will be explained in detail in section 3.3. However, fig. 3 shows the relationship between thiophene HDS activity and the surface area of catalysts after reaction with both different calcination temperature and presulfidation temperature. The good relationship means that the thiophene HDS activity of intermetallic $NdNi_5$ can be well explained by the surface area of catalysts after reaction. The surface area of the catalyst is very seriously affected by the pretreatment conditions of both calcination and presulfidation. Moon and Ihm [19] have reported that Nd has an important role in surface area increase for Nd/Ni bimetals.

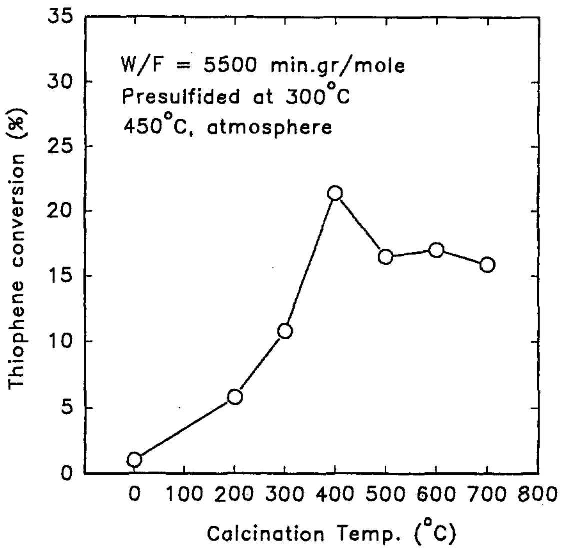

Fig. 1. Thiophene HDS activity of the catalyst calcined at different temperatures and after 200 min reaction.

To investigate the property changes of intermetallic $NdNi_5$, XRD peaks were obtained for all catalysts treated under various conditions. It is thought from results of a TG/DTA experiment that the sulfide catalyst was not oxidized in the XRD measurement in atmosphere at room temperature. By examining the XRD peaks of the calcined catalysts in fig. 4, it was found that $NdNi_5$ starts

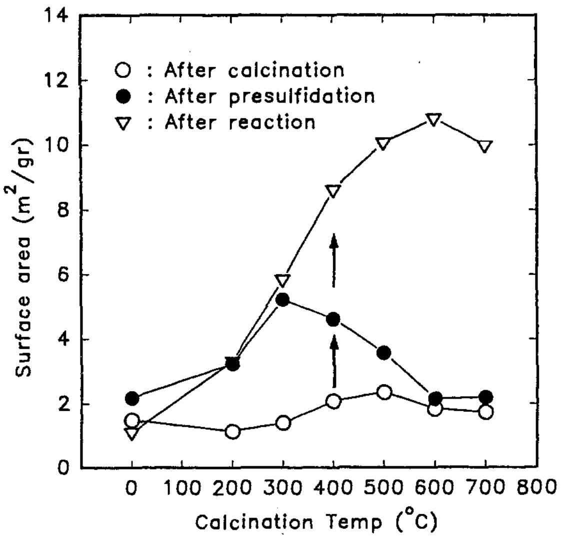

Fig. 2. Surface area variations with different calcination temperatures ((○) after calcination, (●) after presulfidation, (▽) after reaction).

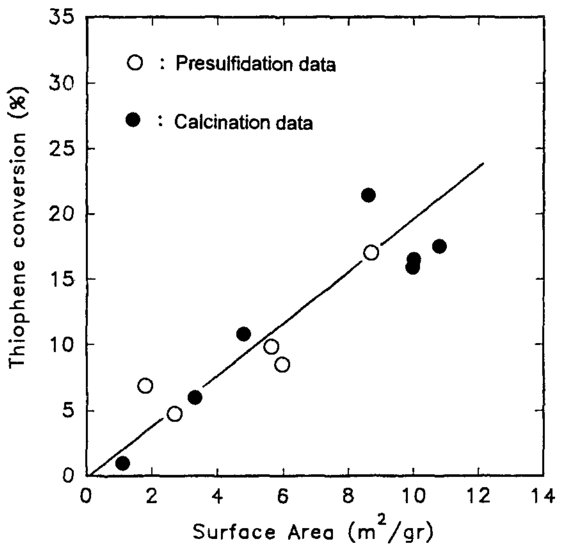

Fig. 3. Correlation between thiophene HDS activity and surface areas of NdNi$_5$ catalysts after reaction ((○) calcined at 600°C with different presulfidation temperatures, (●) presulfided at 300°C with different calcination temperatures).

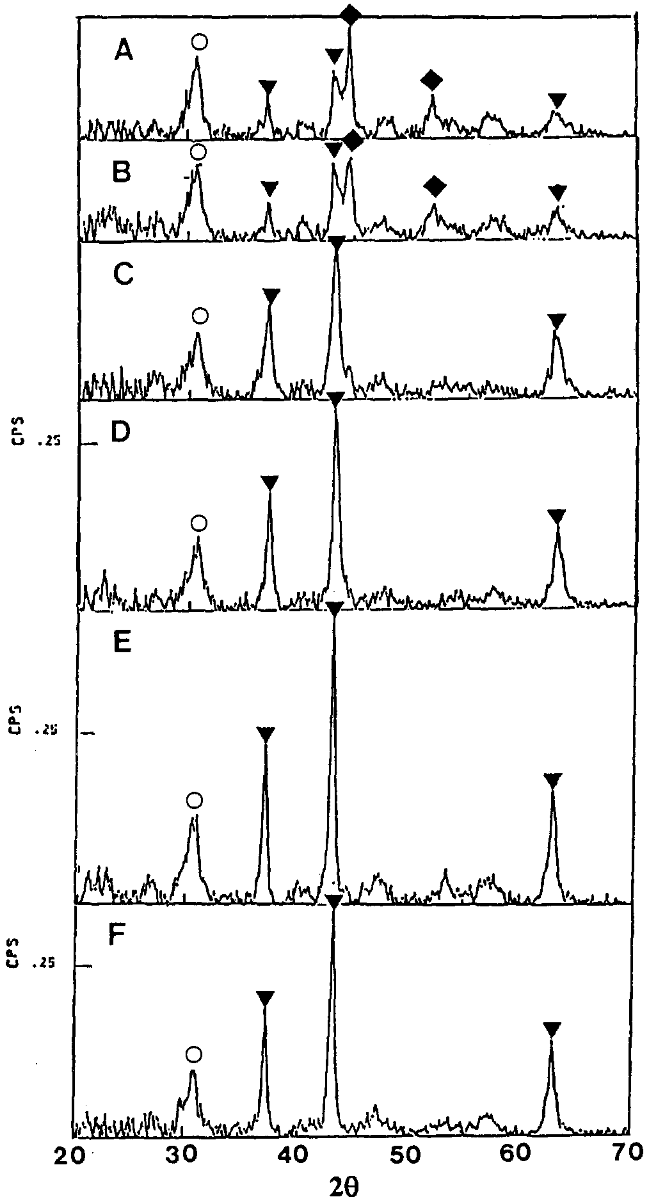

Fig. 4. XRD peaks of NdNi$_5$ in its calcined state at different temperatures. ((A) 200°C, (B) 300°C, (C) 400°C, (D) 500°C, (E) 600°C, (F) 700°C; (○) Nd_2O_3, (▼) NiO, (◆) Ni).

to precipitate to Ni, NiO and Nd_2O_3 at 200°C and fully precipitates to NiO and Nd_2O_3 above 400°C. It is believed that the intermetallic compound was destroyed by calcination and that the full precipitation of intermetallic NdNi$_5$ to NiO has some relation with the high HDS activity of thiophene. This precipitation is likely to develop much more micro-cracks which is responsible for the high surface area after presulfidation and reaction. On the other hand the intensity of the Nd_2O_3 peak is relatively small and nearly constant over all calcination temperatures. Thus Nd_2O_3 is not seriously affected by the calcination conditions [19]. From the XRD peaks of the presulfided catalysts of fig. 5, it is found that the nickel and nickel oxides generated in the calcination step are changed to be nearly amorphous nickel sulfide. Nickel precipitated at a calcination temperature below 300°C is more easily sulfided than nickel oxide. It is thought that the intermetallic NdNi$_5$, which does not fully precipitate into nickel oxide, changes more easily to nickel sulfide without surface area increase because this catalyst skips the oxide state. Nickel oxides having high crystallinity generated above 400°C of calcination changed to be amorphous. When a small oxygen atom is exchanged by a large sulfur atom, nickel oxides are hard to rearrange to crystalline sulfide under the mild presulfidation condition of 300°C. In the presulfidation step catalysts are partially micro-cracked and surface areas slightly increase. The increase of surface area after reaction is more accelerated with increasing calcination temperatures. It is thought that the rearrangement of amorphous sulfide to high crystalline sulfide increases the surface area much more. The high HDS activity of catalysts calcined above 400°C seems the result of surface area increase. XRD peaks of catalysts after 200 min of reaction are shown in fig. 6, in which Ni exists as nickel sulfide (Ni_3S_2) showing high crystallinity and Nd is invisible to XRD. The amorphous nickel sulfide changed to the high-crystalline sulfide and Nd crystal is very fine or amorphous. Shaw et al. had obtained similar results where Ce is invisible to XRD in Cu/Ce alloy [20]. The clue of the changing HDS activity in initial reaction time can be found in the wide difference of XRD peaks between the catalysts after presulfidation and after reaction in figs. 5 and 6.

The SEM photographs of catalysts after calcination, presulfidation and reaction are shown in figs. 7, 8 and 9 respectively. A large crack on the catalysts developed during calcination, as shown in fig. 7, and it is caused by volume increase of oxides. In fig. 8 the crack is much developed by presulfidation. The photographs of the

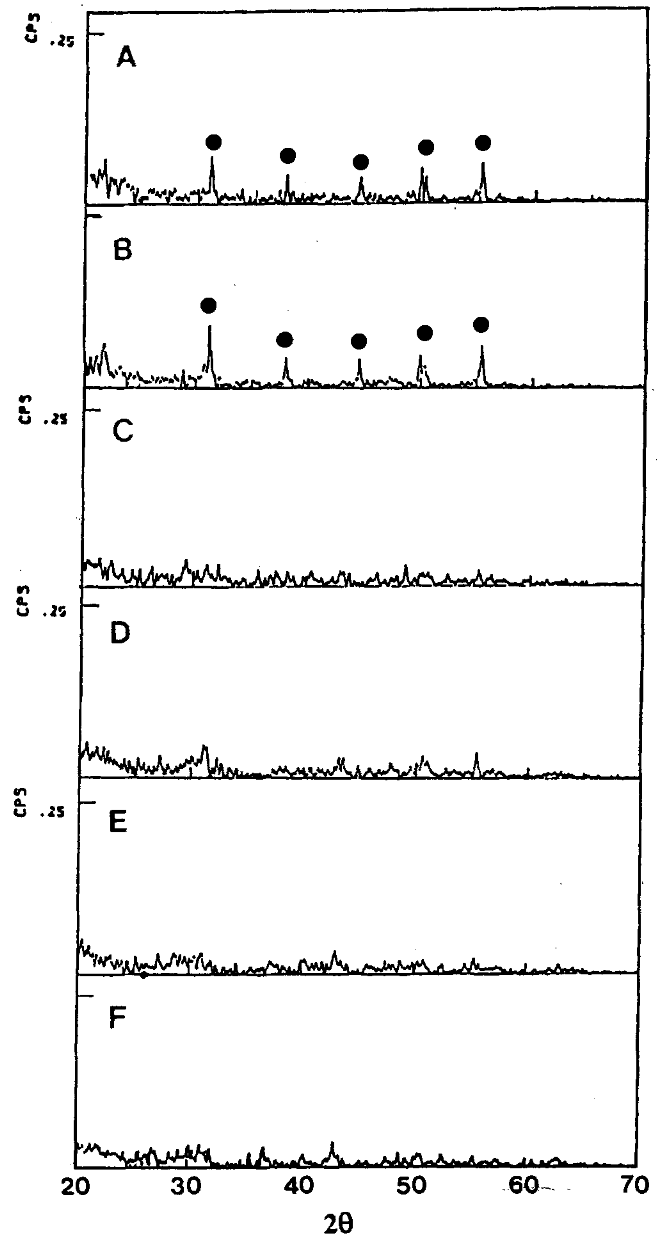

Fig. 5. XRD peaks of $NdNi_5$ in its presulfided state with different calcination temperatures ((A) 200°C, (B) 300°C, (C) 400°C, (D) 500°C, (E) 600°C, (F) 700°C; (●) Ni_3S_2).

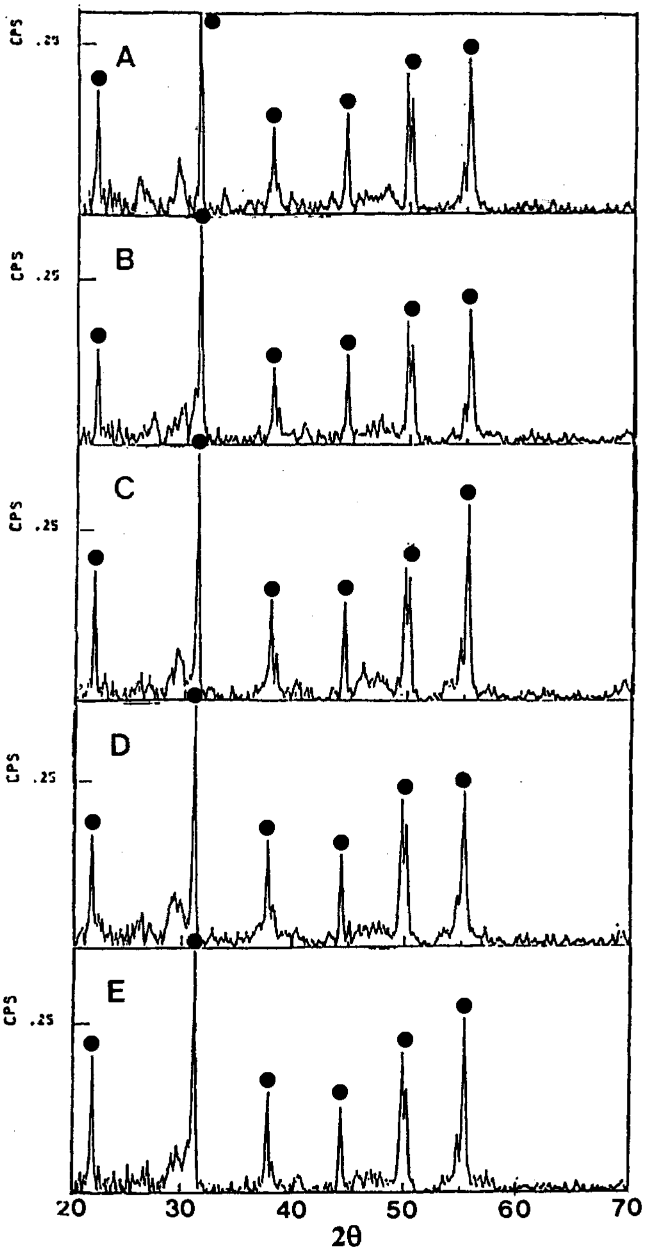

Fig. 6. XRD peaks of $NdNi_5$ in its state after reaction with different calcination temperatures ((A) not calcined, (B) 200°C, (C) 300°C, (D) 500°C, (E) 700°C; (●) Ni_3S_2).

catalyst after reaction in fig. 9 show that the catalyst particle is completely disintegrated and its surface is very clean and smooth because of sintering under the reducing atmosphere of the reaction.

3.2. Presulfidation

Most HDS catalysts are used in the sulfide state and it is well known that the active site of HDS catalysts is the sulfur anion vacancy. Thus the presulfidation condition becomes an important factor in HDS activity. The calcined catalysts were presulfided at various temperatures, including no presulfidation. It seems that the surface of the catalyst is very heterogeneous in initial reaction time and this heterogeneity, which is developed during severe calcination and mild presulfidation, is weakened under the reducing reaction atmosphere with time. The catalyst presulfided above 400°C shows also low HDS activity. This can be explained by the fact that these catalysts have low sulfur anion vacancy and low surface area due to sintering under the high presulfidation temperature. Thus the optimum presulfidation temperature was obtained at 300°C, as presented in fig. 10. The oxygen atom being exchanged for a large sulfur atom during presulfidation, the catalysts are microcracked and their surface areas slightly increase.

The XRD peaks of the catalysts after reaction are shown in fig. 11. Nickel in intermetallic $NdNi_5$ has chan-

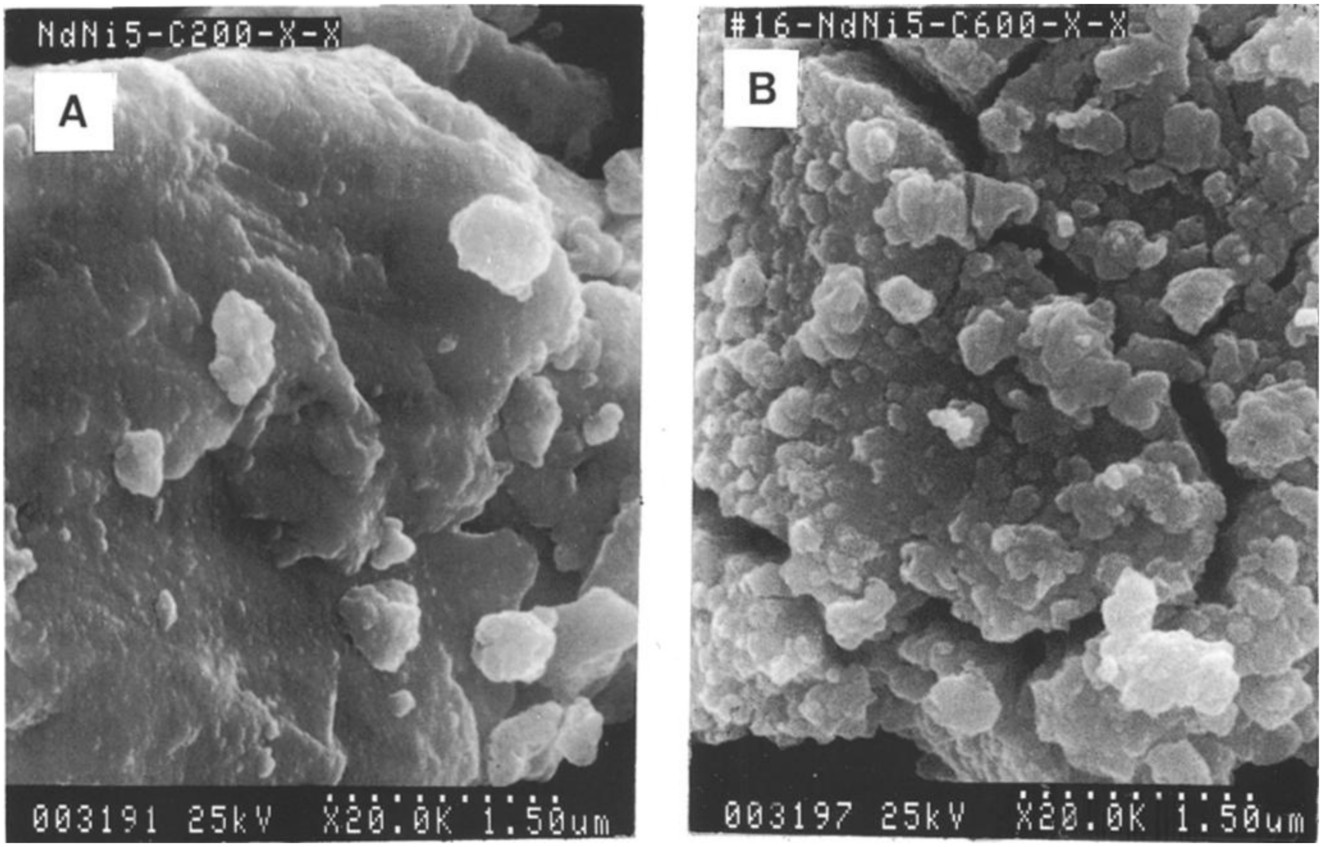

Fig. 7. Scanning electron micrographs of $NdNi_5$ calcined at different temperatures ((A) 200°C, (B) 600°C).

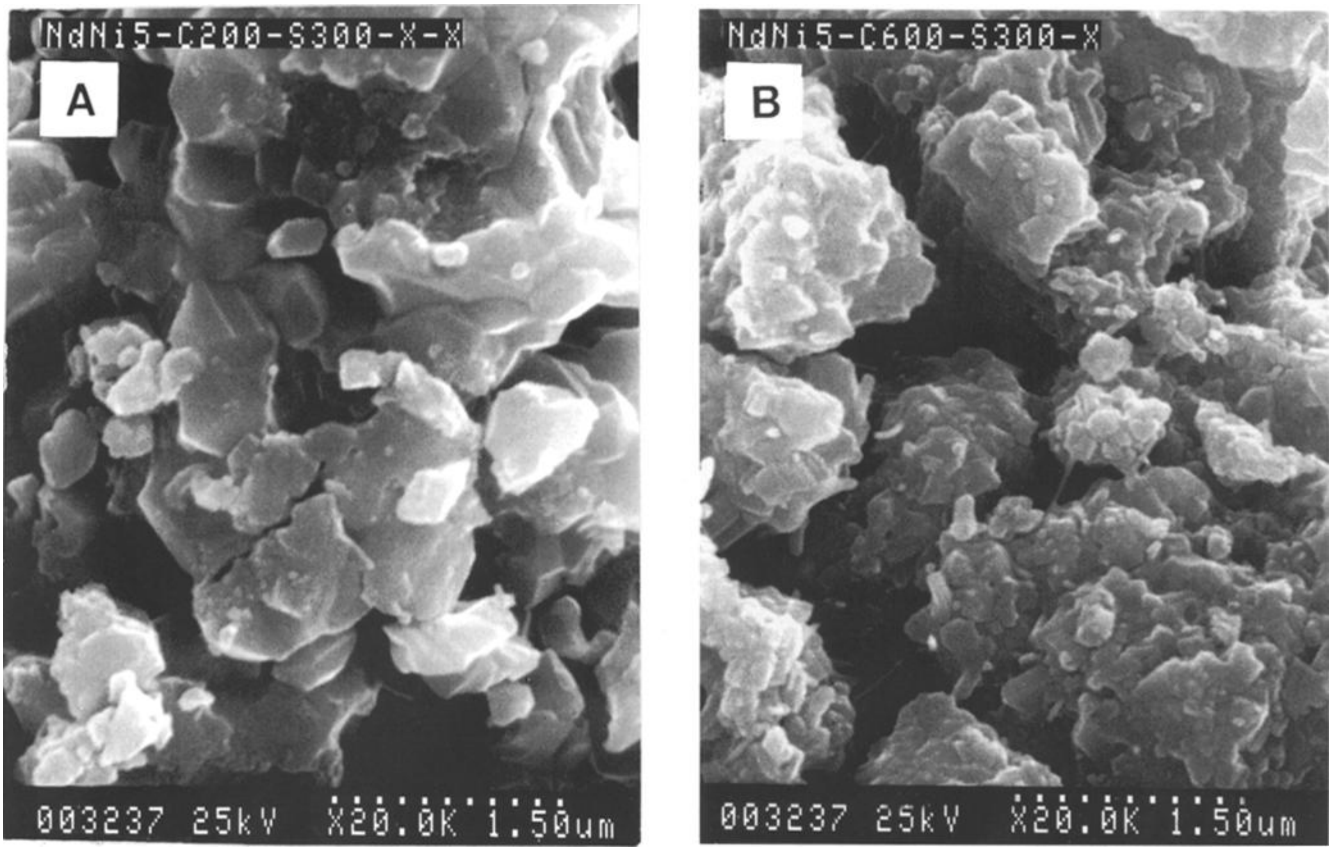

Fig. 8. Scanning electron micrographs of $NdNi_5$ after presulfidation with different calcination temperatures ((A) 200°C, (B) 600°C).

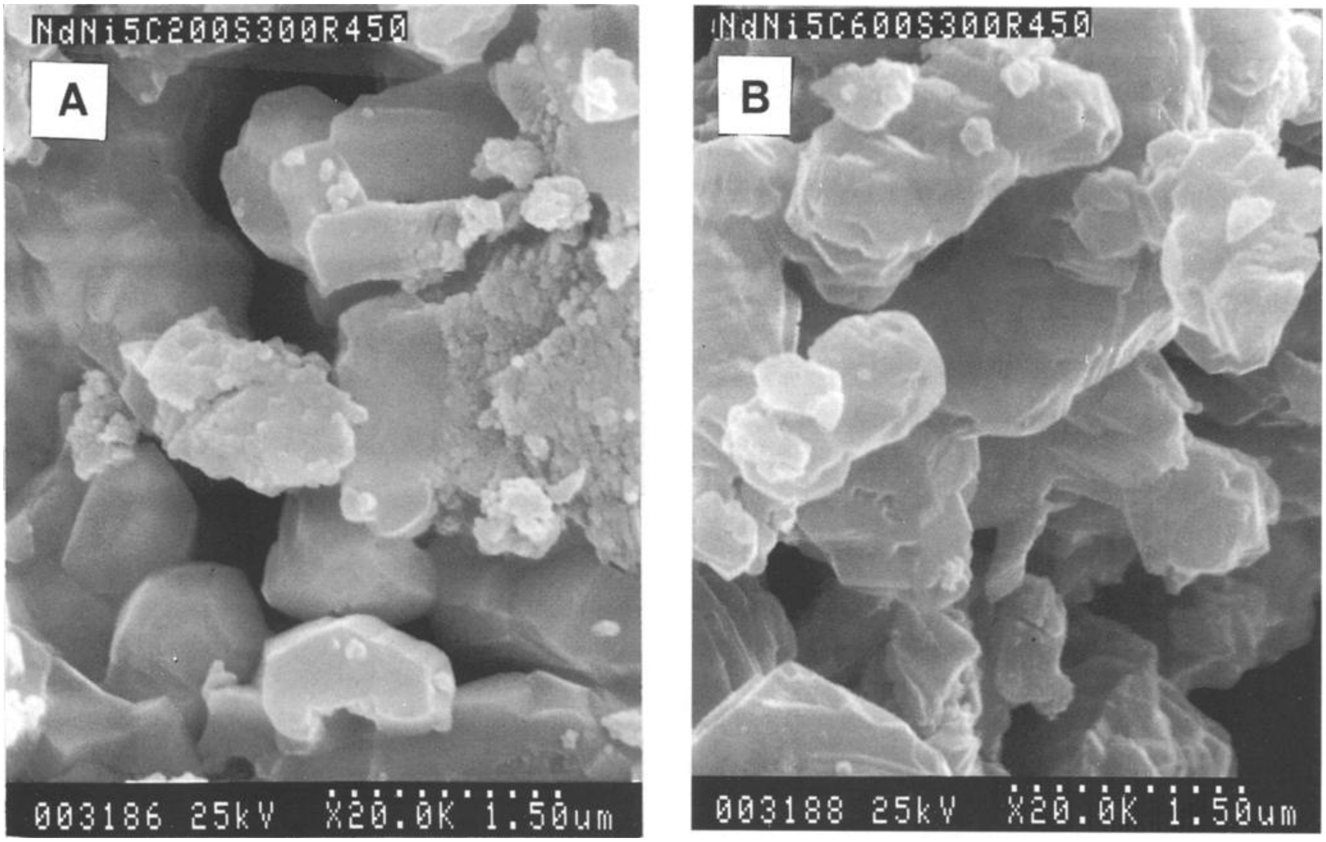

Fig. 9. Scanning electron micrographs of $NdNi_5$ after reaction with different calcination temperatures ((A) 200°C, (B) 600°C).

ged to nickel sulfide (Ni_3S_2) for all presulfidation temperatures including the no presulfidation sample. The catalysts presulfided above 400°C show the XRD peaks originated by Nd. This means that Nd is segregated to a relatively large crystal as Nd_2O_2S and therefore Nd loses the effectiveness to prevent the sintering of Ni. It is believed that Ni_3S_2 is the active site of thiophene HDS and Nd works as a structural promoter [19]. Fig. 3 presents the relationship between thiophene HDS activity and surface area.

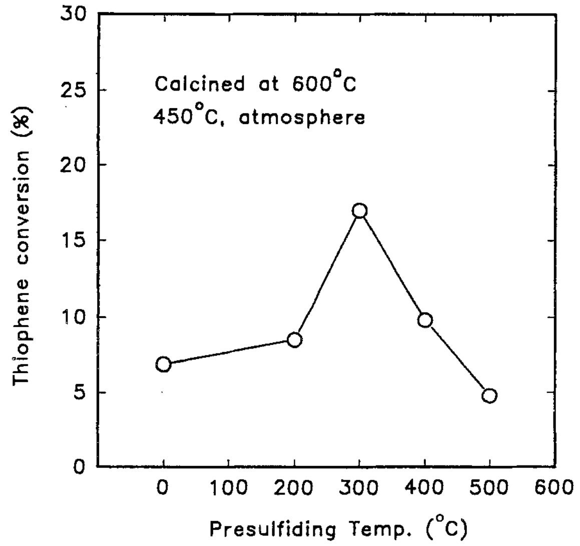

Fig. 10. Thiophene HDS activity after 200 min with different presulfidation temperatures.

Conclusively, the effect of presulfidation as well as calcination on the HDS activity is well explained by the surface area of the catalysts and intermetallic $NdNi_5$ is destroyed and recrystallized to sulfide after reaction.

3.3. A model for the surface area increase

Recently it was reported that La_2O_3 acts as a support in ethane hydrogenolysis and its role was explained as a decoration model [21]. On the basis of our results, a model for the surface area increase of intermetallic compounds during pretreatment and reaction is summarized below and depicted in fig. 12. The model for the surface area increase is also macroscopically supported by SEM photographs, although it is difficult to interpret the surface area of catalysts with SEM photographs because the surface of catalysts is more microscopic than the SEM photograph.

(1) *Calcination step:* The intermetallic compound $NdNi_5$ precipitates to NiO and Nd_2O_3 (fig. 4). These oxides seem to be the precursors which will develop the high

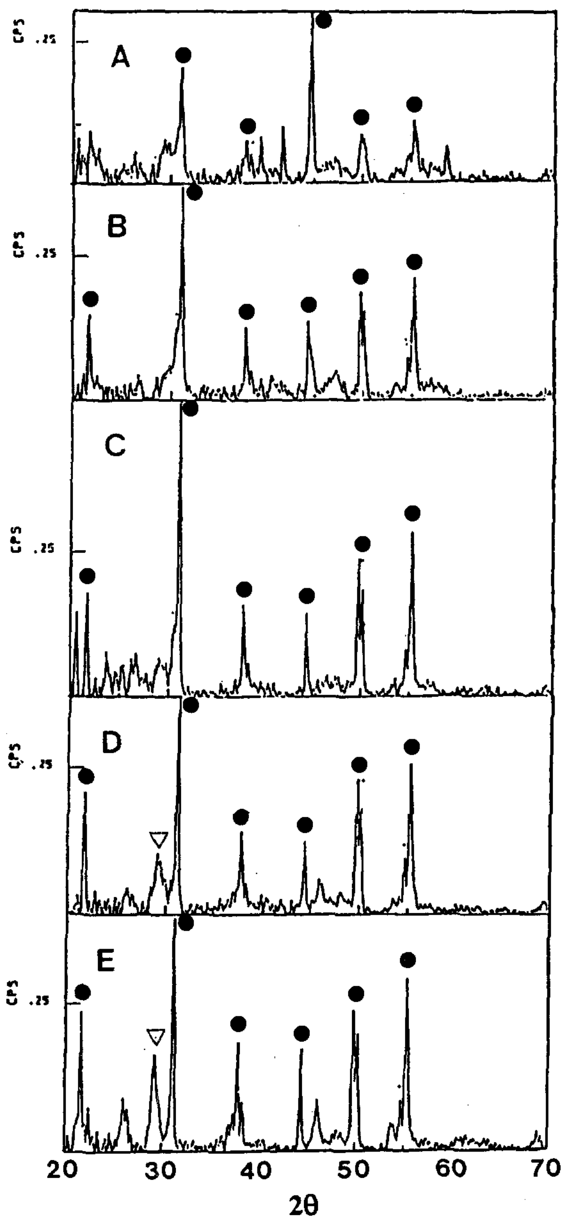

Fig. 11. XRD peaks of $NdNi_5$ in its state after reaction with different presulfidation temperatures ((A) not presulfided, (B) 200°C, (C) 300°C, (D) 400°C, (E) 500°C; (●) Ni_3S_2, (▽) Nd_2O_2S).

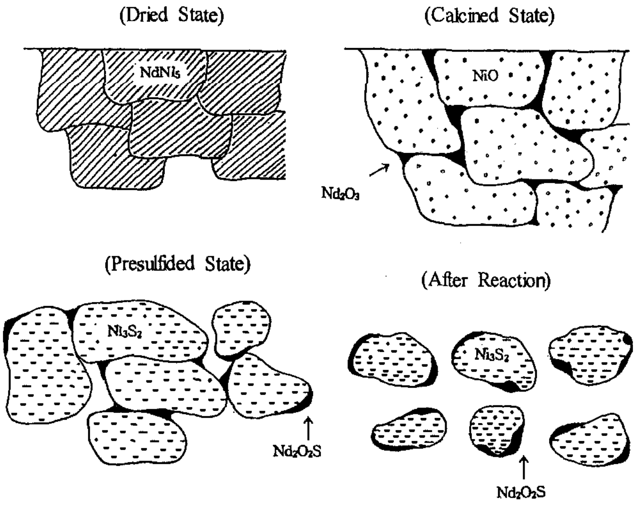

Fig. 12. A model for the surface increase of intermetallic $NdNi_5$ during calcination, presulfidation and reaction.

surface area after presulfidation and reaction. The particle is macro-cracked and its surface is coarse (fig. 7).

(2) *Presulfidation step:* Nickel oxide having high crystallinity changes to nearly amorphous nickel sulfide (fig. 5). In exchanging the small oxygen atom by a large sulfur atom, the catalyst loses its crystallinity and becomes amorphous. In this process the catalyst is micro-cracked (fig. 8) and its surface area increases slightly.

(3) *Reaction step:* The amorphous nickel sulfide changes to high-crystalline nickel sulfide under reducing atmosphere and high temperature (fig. 6). During this rearrangement to high crystallinity, the micro-crack is fully developed and the catalyst is disintegrated to fine particles (fig. 9). Thus its surface area increases much more.

4. Conclusion

The intermetallic compound $NdNi_5$ is disintegrated to fine powder and recrystallized to oxide and sulfide by calcination, presulfidation, and reaction. Its surface area after reaction increased by about 7 times as compared to its original state. The HDS activity of the unsupported catalyst is well correlated with its surface area which is seriously varied with calcination and presulfidation temperature. Ni_3S_2 in intermetallic $NdNi_5$ is the active site of HDS and Nd_2O_2S works as a structural promoter preventing the nickel sintering.

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