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CVD preparation of alumina-supported niobium nitride and its activity for thiophene hydrodesulfurization

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Abstract

Niobium nitride was synthesized on a Si(400) substrate and a γ-alumina pellet using a CVD method with a stream of $NbCl_5$/Ar, NH_3, and H_2 gases at 723–973 K under reduced pressure. The composition and surface properties of the deposited niobium nitride were analyzed using XRD and XPS measurements. The activity of alumina-supported niobium nitrides for the hydrodesulfurization (HDS) of thiophene at 673 K and atmospheric pressure was determined. The alumina had a surface area of 177 $m^2\,g^{-1}$ and the alumina-supported niobium nitride catalyst had surface areas of 179–190 $m^2\,g^{-1}$. Although the catalysts had low activity in the initial stages, the activity increased after 200–300 min started to about three times the initial activities. XPS analysis indicated that the activity of the niobium nitride catalysts was decreased by sulfur accumulation on the surface and nitrogen released from niobium nitride. The relationship between the surface properties of the niobium nitride catalysts and the activities for thiophene HDS is discussed. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Chemical vapor deposition; Hydrodesulfurization; $NbCl_5$; Niobium nitride; Supported catalyst; Thiophene

1. Introduction

New preparation methods of supported catalysts have been studied to develop materials with high activity and selectivity. The chemical vapor deposition (CVD) technique is a useful method for the preparation of high metal loading substances on the surface of support. CVD was originally employed to synthesize high conductivity materials on silicon in the large scale integrated circuit (LSI) field. Niobium nitride was synthesized on silicon by CVD using a stream of $NbCl_5$, N_2, and H_2 [1,2] and $NbCl_5$, NH_3 and H_2 [3,21,22], liquid NH_3 [4], and NH_3 and $Nb(NEt_2)_4$ and $Nb(NMe_2)_5$ [5]. By forming a thin film on a high surface area support, not only an increase in surface area but also the generation of active sites having novel function is expected [6–8]. Recently, thin films of metal nitrides and carbides dispersed on oxide supports have attracted much attention as catalysts [9–11]. Nagai and co-workers [9,10] studied the preparation of alumina-supported molybdenum carbides at 973 K using the CVD technique under reduced pressure, and reported that carbide catalysts obtained by CVD were 3 and 15 times more active per molybdenum content than an impregnated Mo/Al_2O_3 carburized at 973 K and reduced at 673 K, respectively, for the hydrogenation of CO_2.

Niobium sulfide is active for hydrocracking and hydrotreating of petroleum feedstocks. Breysse et al. [12] studied sulfided Nb/Al_2O_3 and Nb/SiO_2 catalysts for their activities in the hydrodesulfurization (HDS) of thiophene and reported a positive relationship

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between HDS activity and the dispersion of niobium on the support. Datka et al. [13] reported that the HDS activity of sulfided and oxidized NbO_3/zeolite catalysts depended on the dispersion of niobium on the surface. Furthermore, Schwartz and Oyama [14] prepared niobium oxynitride by a temperature-programmed synthesis method and reported that the niobium oxynitride had moderate and stable hydrodenitrogenation activity over a period of 60 h. However, little attention has been paid to the surface properties and HDS activity of niobium nitride. In this study, therefore, the niobium nitride catalysts were synthesized on alumina using the CVD method. The surface composition and property of niobium nitride was determined by XPS and XRD analysis. The relationship between the surface properties of the niobium nitride catalysts and the activities for thiophene HDS is discussed.

2. Experimental

2.1. *CVD synthesis of NbN film on Si(400) and alumina*

The CVD experimental apparatus is described in detail elsewhere [6,8]. The system consisted of gas delivery lines, a $NbCl_5$ feed system, a reactor, and a vacuum system. A Si(400) substrate was cleaned by immersion in hydrogen fluoride solution and then rinsed with deionized water. Each substrate was put on a ring-type carbon susceptor in the reactor. The CVD system was evacuated at 0.01 kPa and then purged with argon three times at room temperature. The substrate was reduced with hydrogen at 1073 K for 1 h to remove surface oxides and was cooled to the desired temperature at 0.13 kPa in flowing hydrogen. The $NbCl_5$ was introduced to the reactor by vaporization at 383 K (16 Pa) in an argon stream. Deposition began by directing the argon flow over the $NbCl_5$ source at a flow rate of 10 ml min^{-1} with NH_3 (5 ml min^{-1}) and hydrogen (5 ml min^{-1}) ($NbCl_5$:NH_3:H_2=1:167:167) at a total flow rate of 20 ml min^{-1} in vacuum (0.13 kPa) at temperatures from 773 to 973 K. After each deposition the films in the reactor were allowed to cool slowly to room temperature under argon flow. The substrates were subsequently kept in a desiccator. For the preparation of niobium nitride films to be tested as catalysts, the niobium nitrides were synthesized by CVD on γ-alumina using the ring-type susceptor without carbon. For the activity and XPS measurements, a glovebag was used to transfer the niobium nitride catalyst to a measuring cell attached with each apparatus without exposure to air. The deposition on γ-alumina was carried out at 823 K in a gas mixture of $NbCl_5$–NH_3–H_2 at the same conditions described previously.

2.2. *Characterization*

Powder X-ray diffraction were collected on a Rigaku X-ray diffractometer operating with a scanning speed of 2° min^{-1} from $2\theta=5°$ to 120° with Ni-filtered Cu Kα radiation (λ=1.5418 Å). XPS analysis was performed with an ESCA-3200 spectrometer using Mg Kα radiation (1253.6 eV, 8 kV, 20 mA) with a cylindrical mirror analyzer operating in constant pass energy mode (75 eV). Binding energies were referenced to C15 at 284.5 eV. The specific surface area of the sample was measured on the Coulter 100CX after evacuation of the sample at 473 K and 1×10^{-4} Pa for 2 h. The amount of niobium was analyzed quantitatively by a Shimadzu atomic absorption analyzer after the samples were decomposed in aqua regia.

2.3. *Activity measurement*

The flow system for the HDS of thiophene is described elsewhere [15]. Briefly, the system consisted of a single-pass, differential microreactor at 673 K at atmospheric pressure. Thiophene was introduced into the reactor by bubbling a stream of pure hydrogen at a rate of 10 ml min^{-1} through a thiophene saturator, maintained in an ice bath at 273 K. The concentration of thiophene in the feed stream at a total flow rate of 15 ml min^{-1} was maintained at approximately 3.2×10^{-4} mol l^{-1} through the saturator. Quantitative analysis was performed by injecting a sample from a sampling loop into the gas chromatograph to analyze the amount of thiophene (column: 10% Silicon DC-550) at 348 K and the reaction products (column: VZ-8) at 313 K. The rate of thiophene HDS is given by

$$\text{HDS rate} = FXC_{\mathrm{T}}/\mathrm{m}^2\text{-cat.}\ (\mathrm{nmol\,m^{-2}\,s^{-1}})$$

where F is the total flow rate of the feed, X the fractional conversion, C_T the concentration of thiophene in the feed, and m^2-cat. the catalyst surface area.

3. Results and discussion

3.1. CVD film preparation on a Si(400) substrate

In order to determine the optional condition for synthesizing niobium nitride on alumina, niobium nitride films were first synthesized on a Si(400) plate using various deposition temperatures. These films were analyzed using XRD. The deposition of niobium nitrides was performed at 723–973 K in a gas mixture of $NbCl_5/Ar–NH_3–H_2$ at a total pressure of 0.12 kPa. The X-ray diffraction patterns of the niobium nitride films on the Si(400) substrate are shown as a function of deposition temperature in Fig. 1. The XRD results show that only NbN was formed. The NbN film prepared at 773 and 873 K showed strong (200) lines, but the NbN film deposited at 823 K gave a weaker line. The growth rate of niobium nitride films as a function of deposition temperature is shown in Fig. 2. The largest film growth rate was 2.3 µm min^{-1} for the niobium nitride film deposited at 823 K and 0.5 µm for the catalysts below 773 and above 873 K. Although the crystallite size (NbN(200)) of the niobium nitride films deposited at 773 and 873 K was 1.9 nm, the crystallite size for the 823 K-deposited niobium nitride was 1.5 nm. From these results, it was concluded that the 823 K-deposited film had small particles of NbN which were partly amorphous. Therefore, the alumina-supported niobium nitride catalyst was synthesized at 823 K, the optimum deposition temperature for obtaining a high surface area material.

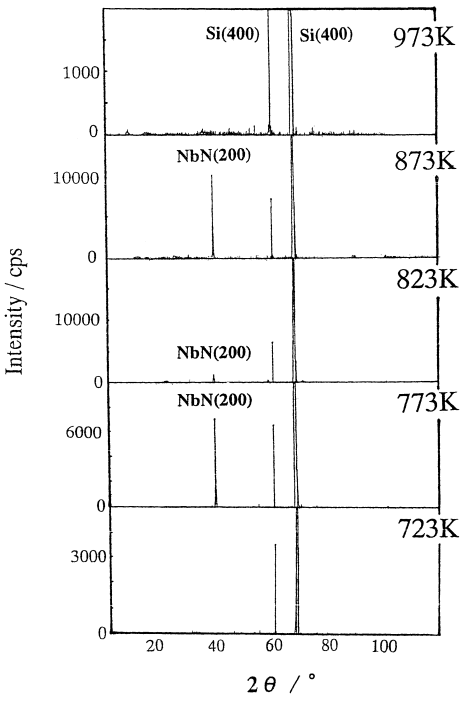

Fig. 1. X-ray diffraction patterns of niobium nitride films deposited on Si(400) substrate for 60 min as a function of deposition temperature.

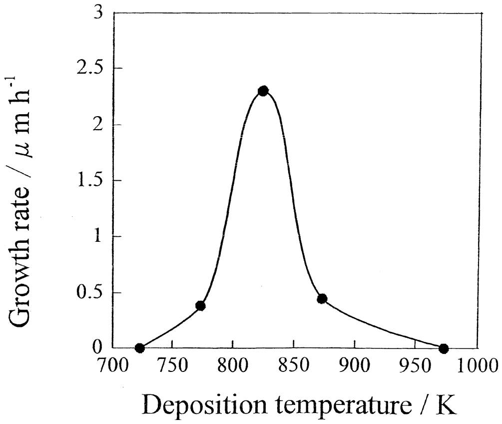

Fig. 2. The deposition rate of niobium nitride films on Si(400) substrate for 60 min as a function of deposition temperature.

3.2. Deposition of niobium nitride on alumina

Fig. 3 shows SEM images of niobium nitride deposited on alumina pellet at 823 K using different reaction times. Dense, uniform and lustrous films were formed. At 15 min, in the initial stages, 0.5 µm fine round particles were formed, and at 30 and 60 min the niobium nitride crystals agglomerated and grew to larger, irregular round particles of 2–3 µm. Round particles with needles were formed on the nitride particle near the alumina support. The surface roughness of the particles increased with increasing deposition time, but the SEM images indicated a smooth transition in the formation of the niobium nitride from

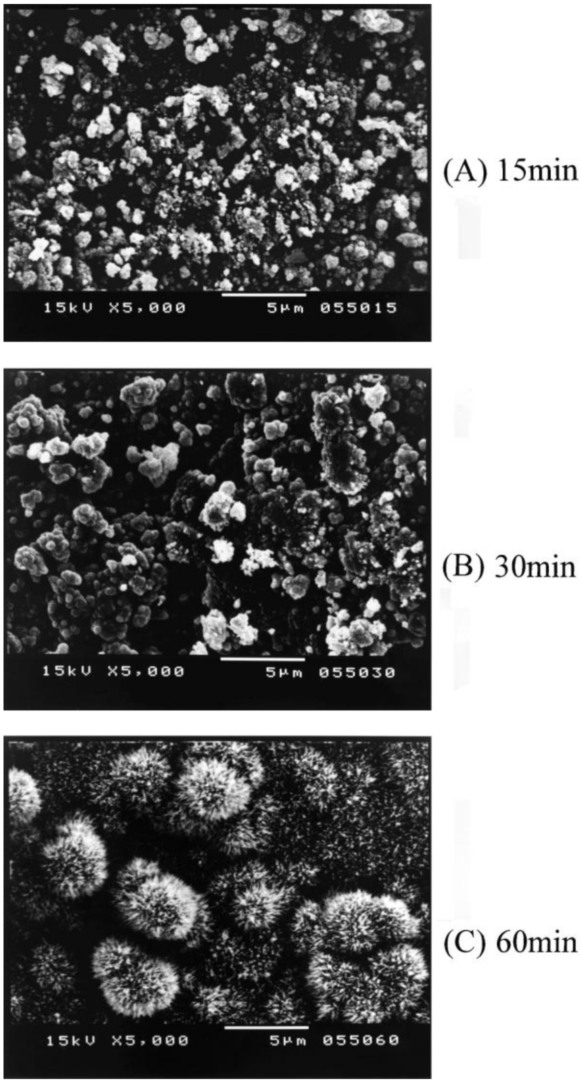

Fig. 3. SEM images of the alumina-supported niobium nitride catalysts deposited at 823 K for (A) 15; (B) 30 and (C) 60 min.

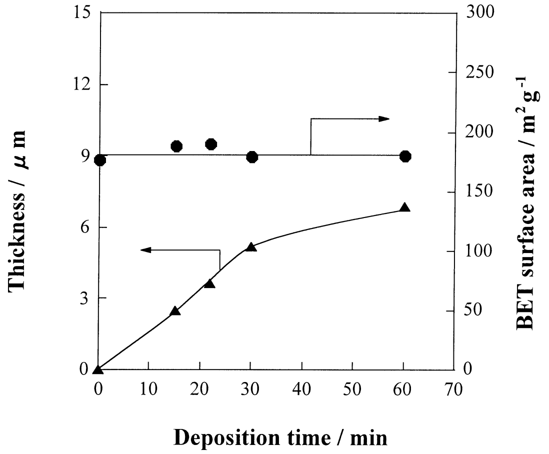

Fig. 4. Film thickness and BET surface area of the alumina-supported niobium nitride catalysts deposited at 823 K with deposition time.

initial to final stages. The change in thickness and BET surface area of niobium nitride catalysts deposited at 823 K as a function of deposition time is shown in Fig. 4. The film thickness increased with preparation time at a constant growth rate of 0.18 μm min^{-1} up to 30 min and then more gradually up to 60 min. The BET surface area was almost constant although the film thickness increased, indicating that niobium nitride covered the outer surface of the alumina. The micro and mesopore distribution of the catalyst varying with deposition time was analyzed by the HK method for 0.4–2.2 nm and by the BJV method for 4–45 nm pore size and the results are shown in Fig. 5. Approximately 0.7–0.9 nm micropores on alumina gradually decreased up to 30 min and then 0.6 nm mesopore sizes increased with deposition time from 30 to 60 min. It is likely that the deposition of niobium nitride initially plugged the micropores on alumina and then formed finer micropore on the nitride layer itself.

The XPS spectra of Nb 3d and N 1s for niobium nitrides deposited on the Si(400) substrate are shown in Fig. 6. The XPS binding energies of the Nb 3d$_{5/2}$ lines were observed at 206.6 and 206.9 eV from 773 to 873 K. This suggests the formation of NbN on the Si(400) plate. Prieto et al. [16] reported that for $x>0.7$ in NbN$_x$ when the binding energy of the Nb 3d$_{5/2}$ was more than 206.3 eV. Also, the Nb 3d$_{5/2}$ binding energy was reported to be 207 eV for NbN powders [17,23]. Furthermore, the Nb 3d$_{5/2}$ binding energies of 206.6 and 206.9 eV for the NbN powder are significantly higher than the values reported for NbN$_{0.9}$ film (204 eV: N 1s; 397.3 eV) [5,18]. From this, it is inferred that niobium nitrides were deposited on alumina as powders. The Nb 3d peak for the film deposited at 973 K appeared at 202.7 eV which is indicative of Mo metal.

The N 1s spectra showed a main peak at 397.5–397.7 eV for the samples prepared at 773–873 K.

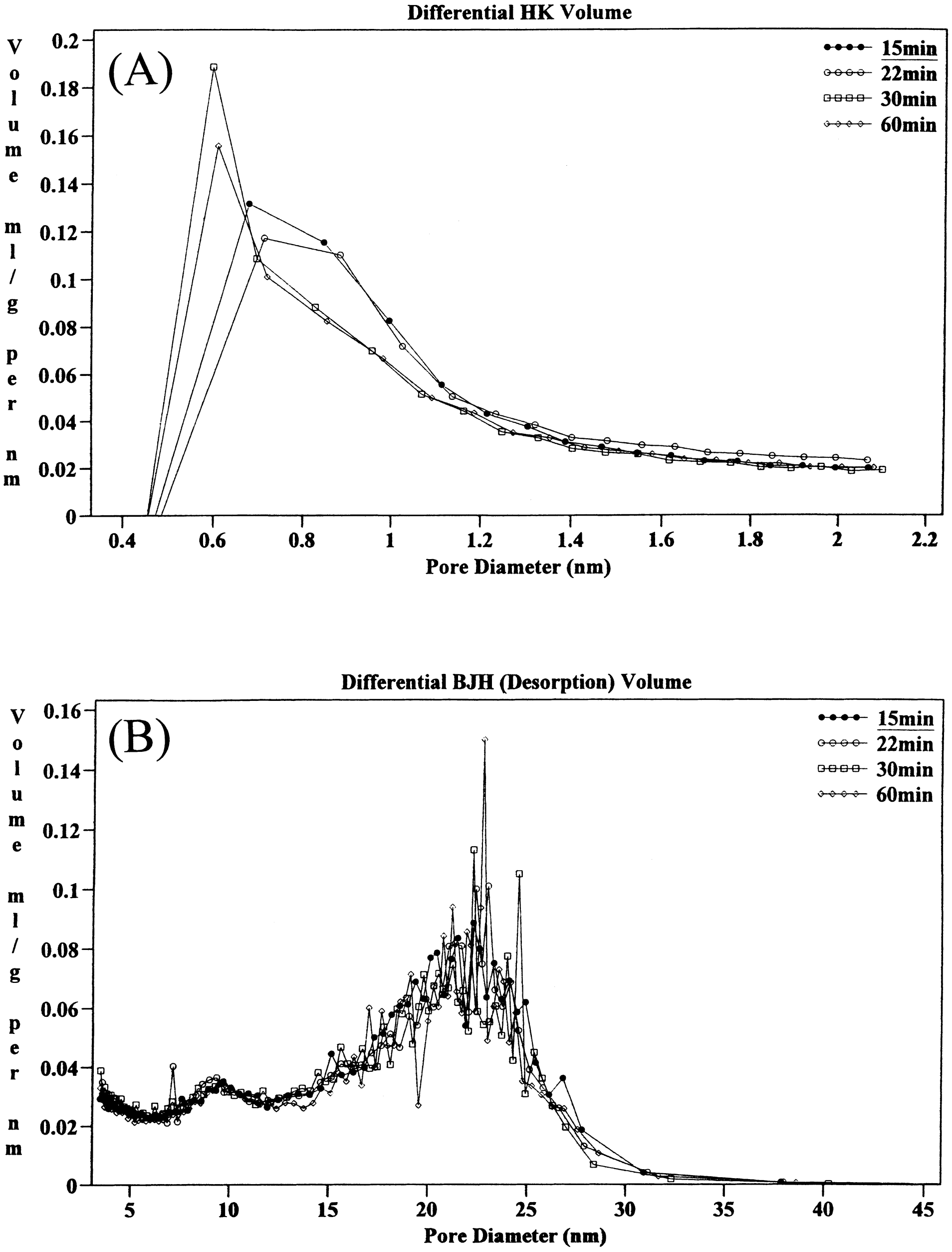

Fig. 5. Pore size distribution (A: 0.4–2.2 nm, B: 5–40 nm) of the alumina-supported niobium nitride with deposition time.

The N 1s binding energy was reported to be 397.2–397.4 and 397.6 eV for a NbN film [5,17,18,23], and 397.5 eV for NbN on silicon substrate [17,23]. The peak at 397.2 eV was attributed to $N^{\delta-}$, a species with the nitride ion character. The Nb 3d peaks of the deposited niobium nitride were shifted to higher binding energies and the N 1s peaks were shifted to a lower position. The shifts were larger at lower deposition temperature. It is likely that the direction of electron transfer is from niobium to nitrogen. The atomic ratios of the XPS Nb 3d/Al 2p and N 1s/Nb 3d for the alumina-supported niobium nitride catalysts

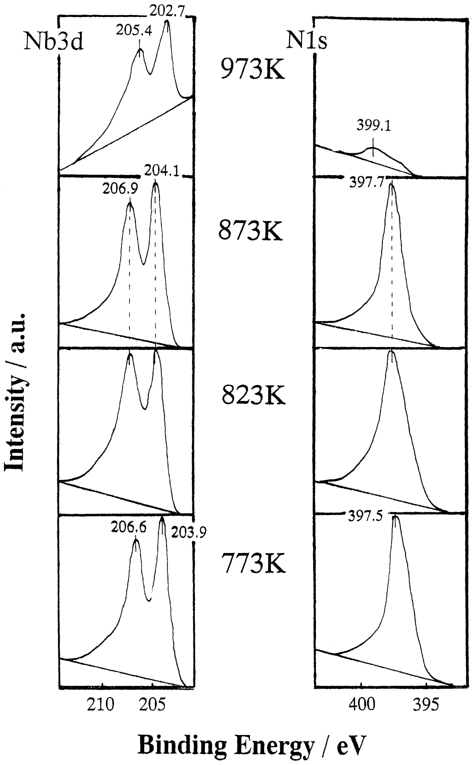

Fig. 6. XPS spectra on Nb 3d and N 1s regions of the niobium nitride catalyst deposited on γ-alumina.

as a function of deposition time and before reaction are shown in Fig. 7. The Nb/Al atomic ratio increased with deposition time in the same manner as the thickness of niobium nitride as shown in Fig. 4. The N/Nb atomic ratios for all deposition times were constant at N/Nb=1.

3.3. HDS of thiophene and active sites

The reaction products in the HDS of thiophene on the alumina-supported niobium nitride catalysts at 673 K were butenes and butane but not tetrahydrothiophene nor butadiene. Fig. 8 shows the activities of the catalysts in the HDS of thiophene at 673 K and atmospheric pressure. The activity of the catalysts was low at the initial stages of the reaction up to 100–200 min, but increased over about 80 min to a steady value. The HDS rates for the niobium nitride catalysts in the initial stages of the reaction are plotted against the atomic ratio of the XPS Nb 3d/Al 2p before reaction in Fig. 9. The HDS rate was higher for the lower niobium content catalysts. The nitrogen content was constant (N/Nb ratio of 1) as shown in Fig. 7. After reaction, the catalyst was analyzed using XPS measurements to determine whether or not niobium sulfide was formed during the reaction. XPS S 2p signals [19,20] were observed in the spent catalyst after the catalyst, indicating that the catalyst was sulfided during the reaction. The HDS rate for the nio-

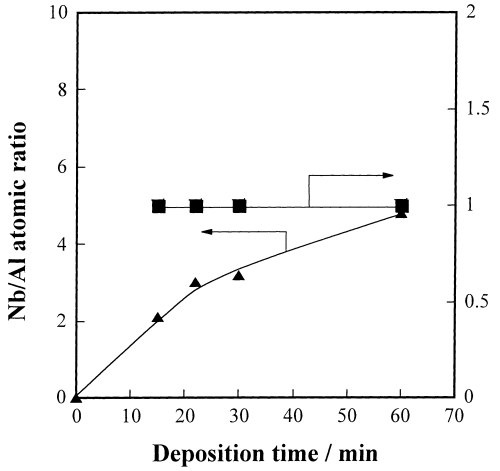

Fig. 7. The atomic ratios of XPS Nb 3d/Al 2p and N 1s/Nb 3d of the niobium nitride catalysts before the reaction as a function of deposition time.

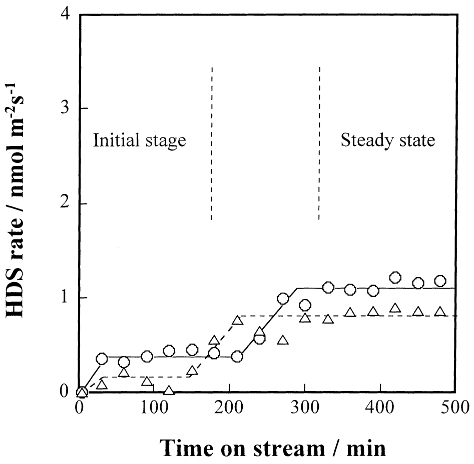

Fig. 8. The HDS of thiophene on the alumina-supported niobium nitride catalysts deposited at 823 K in (○) 15 and (△) 22 min in the initial stages and steady state of the reaction at 673 K.

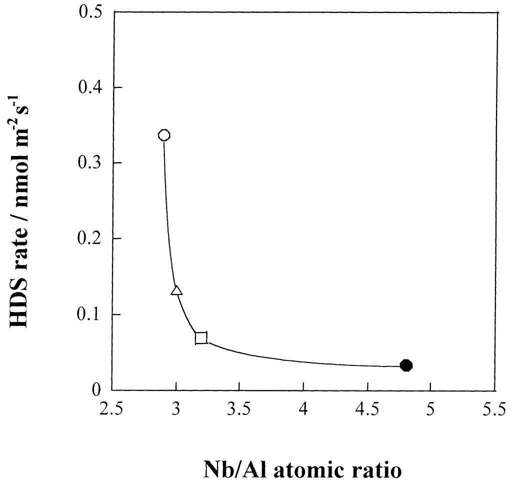

Fig. 9. The rates in thiophene HDS at 673 K as a function of the atomic ratio of the XPS Nb 3d/Al 2p after the reaction for the CVD catalysts deposited for (○) 15; (△) 22; (□) 30 and (●) 60 min.

bium nitride catalysts as a function of the S 2p/Al 2p atomic ratio is shown in Fig. 10. The HDS rate for the catalysts at the steady state decreased with increasing S 2p/Al 2p atomic ratio, indicating that sulfur had a poisoning effect on the activity. This seems to be contrary to the results of the group of Breysse who report that niobium sulfide is a good catalyst for HDS [12]. The difference in the HDS rate in the initial stages and the steady state of the reaction is plotted against the difference in the N/Al atomic ratio before and after reaction in Fig. 11. The difference in HDS rate decreased with increasing difference in the N/Al atomic ratio. Since the composition of niobium nitride did not change before and after the reaction, the difference in the N/Al of 1.4 before and after reaction was due to the release of adsorbed nitrogen (NH_x) or dissolved nitrogen in the catalysts. Furthermore, the release of nitrogen (N/Al from 1.4 to 4.2) was attributed to the loss of nitrogen from niobium nitride to form niobium sulfide. Thus, the removal of nitrogen lowered the activity of the niobium nitride catalyst.

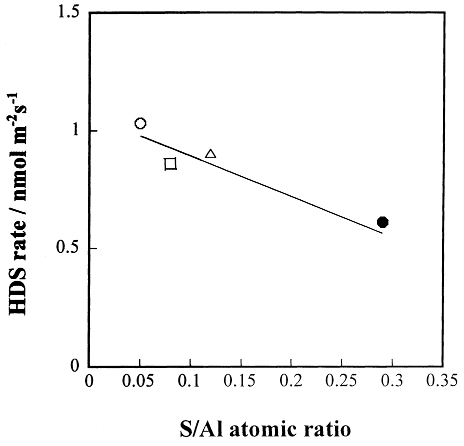

Fig. 10. The atomic ratios of the XPS N 1s/Al 2p and S 2p/Al 2p as a function of the HDS rate at the steady state of the reaction at 673 K. The deposition time is (○) 15; (△) 22; (□) 30 and (●) 60 min.

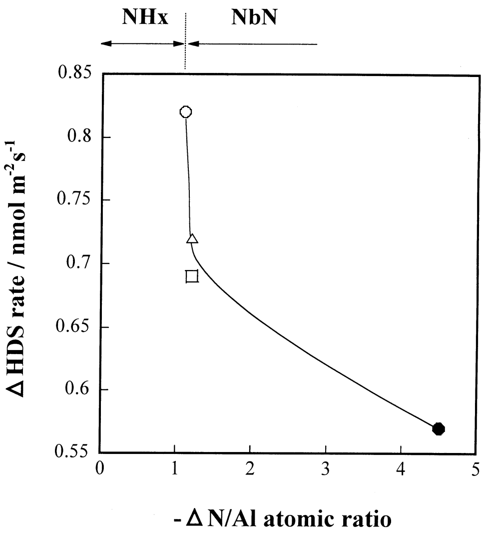

Fig. 11. The difference in the HDS rate at the first stage and the steady state of the HDS reaction at 673 K as a function of the difference in XPS N 1s/Al 2p atomic ratio before and after the reaction. The deposition time is (○) 15; (△) 22; (□) 30 and (●) 60 min.

4. Conclusions

A thin film of niobium nitride was deposited on Si(400) and alumina by the reaction of $NbCl_5$ with NH_3, and H_2 gases at 823 K under reduced pressure. The deposition of niobium nitride initially plugged the micropores on alumina and then continued on the outer surface to produce a uniform film. A peak of highly crystallite NbN (200) phase was observed. Niobium nitride deposited on the alumina was active for thiophene HDS at 673 K and atmospheric pressure. The activity decreased during the reaction by the loss of nitrogen from the catalyst at its replacement by sulfur.

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