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

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Abstract

Tungsten nitride was synthesized on γ-alumina pellet and quartz plate using the chemical vapor deposition (CVD) method in a stream of WCl_6, NH_3, H_2 and Ar gases at 700°C under reduced pressure. The effects of the supports, catalyst preparation and pretreatment on the activities of alumina-supported tungsten nitrides for the hydrodesulfurization (HDS) of thiophene at 300°C and atmospheric pressure were discussed. The alumina-supported tungsten nitride catalyst prepared by the CVD method had a surface area of 161 $m^2 g^{-1}$. The micropore distribution of the alumina-supported CVD catalyst varying with deposition time was analyzed by Dolimore–Heal method. The surface area of the CVD catalysts depended on the supports such as alumina, quartz, and zeolite Y. Thiophene HDS showed a constant activity of the CVD/alumina catalysts deposited for 30 and 60 min, but the 90 min-deposited catalyst was activated after the decreased activity at an initial stage. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemical vapor deposition; Hydrodesulfurization; Supported catalyst; Tungsten nitride; WCl_6

1. Introduction

New preparation methods of supported catalysts have been researched to develop a catalyst with high activity and selectivity. Chemical vapor deposition (CVD) technique is a useful method for the preparation of high metal loading on the surface of the catalyst. CVD is originally a synthesis method of high conducting materials on silicone in the LSI field [1–4]. Recently, thin films of metal nitrides and carbides dispersed on oxide supports have attracted much attention as catalysts. By forming a thin film on high-surface area support, not only an increase in the surface area of the thin film but also the generation of active sites having novel function is expected. Nagai and coworkers [5,6] studied the preparation of alumina-supported molybdenum carbides at 700°C using CVD technique under vacuum pressure and reported that the CVD carbide catalysts were 3 and 15 times more active per molybdenum loading than the impregnated Mo/Al_2O_3 carburized at 700°C and the 400°C-reduced catalysts, respectively.

Tungsten sulfide is active for hydrocracking and hydrotreatment of petroleum feedstocks. Rao and Dhar [7] studied sulfided W/Al_2O_3 and W/SiO_2 catalysts and their activities of the hydrodesulfurization (HDS) of thiophene and reported the relationship between HDS activity and the dispersion of tungsten on the support. Cid et al. [8] reported that the HDS

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activity of sulfided and oxidized WO_3/zeolite catalysts depended on the dispersion of tungsten on the surface. However, little attention has been paid to the catalytic properties and preparation of tungsten nitride. In this study, therefore, the tungsten nitride catalysts were synthesized on supports using the CVD method. The effect of the supports and the deposition time on the surface property and its activity for the HDS of thiophene are discussed.

2. Experimental

2.1. CVD apparatus and W_2N film synthesis on quartz substrate

The CVD experimental apparatus is schematically illustrated in Fig. 1. The system consists of gas delivery lines, a WCl_6 feed system, a reactor, and a vacuum system. The quartz substrate was cleaned by immersion in hydrogen fluoride solution and then rinsed with deionized water. Each substrate was put on the ring-type carbon susceptor in the reactor. The CVD system was evacuated at 0.1 Pa and then purged with argon three times at room temperature. The substrate was reduced at 800°C in hydrogen for 1 h to remove surface oxides after the temperature was raised to 680°C at 0.1 Pa in flowing argon. Deposition began by directing the argon flow over the WCl_6 source, heated at 150°C (16 Pa) at a flow rate of 15 ml min^{-1} with NH_3 (20 ml min^{-1}), hydrogen (5 ml min^{-1}) and argon (20 ml min^{-1}) in vacuum (0.12–0.17 kPa) at temperatures of 680°C and 700°C. After each deposition the films were allowed to cool to room temperature slowly in the reactor under argon flow. The substrates were kept in a desiccator afterwards.

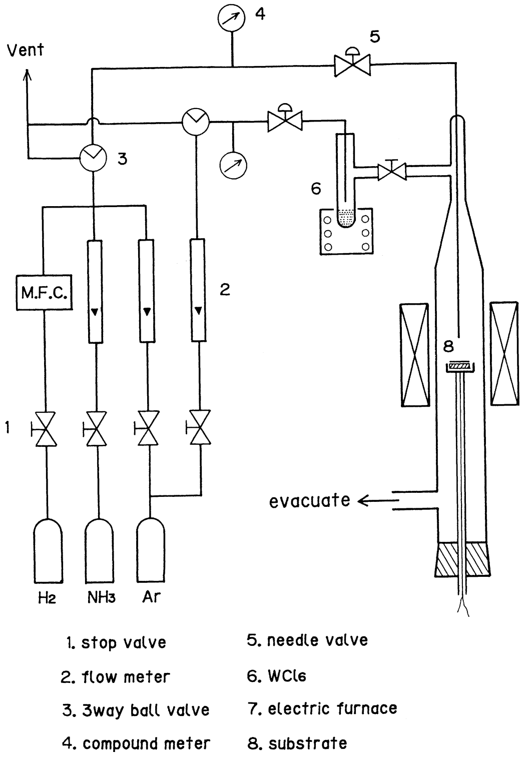


Fig. 1. Schematic diagram of the CVD apparatus.

2.2. CVD catalyst preparation

For preparation of W_2N film as a catalyst, the tungsten nitrides were synthesized on γ-alumina of the ring-type susceptor without carbon and the substrate in the CVD reactor. Quartz sand (10–20 mesh) and zeolite Y particles (10–20 mesh, Japan reference catalyst, JRCAL04) were also used for the support-effect on the activity. The WCl_6 was introduced to the reactor with argon gas by vaporization at 150°C. The deposition was performed at 700°C in a gas mixture of WCl_6–NH_3–H_2 (NH_3:H_2:WCl_5/Ar:Ar=20:5:15:20) at a total flow rate of 60 ml min^{-1} and at a total pressure of 70 Pa.

2.3. Characterization

For measurement of the physical property of the nitrided catalysts such as molybdenum contents and surface area, the nitrided catalysts were passivated in 1.0% O_2 in He at room temperature for 12 h. Since the composition of the sample was changed during TPR, the compositions of the intermediates and final products were measured using XRD. The preparation conditions of the samples were the same as those for the separate TPR experiments. X-ray diffraction powder analysis was performed with Ni-filtered Cu K_α radiation (λ=1.5418 Å) with a Rigaku X-ray diffractometer operating with a scanning speed of 2° min^{-1} from 2θ=5° to 120°. XPS measurements were taken by an ESCA-850 spectrometer using Mg K_α radiation (1253.6 eV, 8 kV, 30 mA) with a cylindrical mirror analyzer operating in constant pass energy mode (75 eV). For preparation of XPS samples, the samples in form of powder were mounted on copper plate with silver-paste. The samples were degassed for 2 h at 200°C in a vacuum oven and then for 1.5 h at room temperature in the prechamber of spectrometer. Binding energies were referenced to Al 2p at 74.7±0.2 eV. The specific surface area of the sample was measured by nitrogen adsorption using a standard BET apparatus after evacuation of the sample at 473 K and 1 Pa for 2 h. Nitrogen contents were measured using a Perkin-Elmer CHN elemental analyzer. The amount of tungsten was analyzed quantitatively by ICP analysis after the samples were decomposed in nitrohydrochloric acid.

2.4. Activity measurement

The flow system for the HDS of thiophene is shown elsewhere [9]. The HDS of thiophene was conducted using a single-pass, differential microreactor at 300°C in atmospheric pressure. Thiophene was introduced into the reactor by bubbling a stream of pure hydrogen at a rate of 15 ml min^{-1} through a thiophene saturator, maintained in an ice bath at 0°C. The concentration of thiophene in the feed stream at a total flow rate of 20 ml min^{-1} was maintained at approximately $3.2\times 10^{-4}\,\mathrm{mol\,l^{-1}}$ through the saturator. Sampling was performed by injecting a sample from a sampling loop into the gas chromatograph for quantitatively analyzing the amount of thiophene (column packing agent: 2% Silicon OV-17) and the reaction products (VZ-8). The rate of HDS of thiophene is given by

$$\mathrm{HDS\,rate} = FXC_\mathrm{T}/W \quad (\mu\mathrm{mol\,g^{-1}\,min^{-1}}),$$

where F is the total flow rate of the feed (ml min^{-1}); X, the fractional conversion; C_T, the concentration of thiophene in the feed (μmol ml^{-1}); and W, the catalyst weight (g).

3. Results and discussion

3.1. CVD film preparation on a quartz-substrate

In order to synthesize tungsten nitride on alumina uniformly, the tungsten nitride film was first synthesized on quartz plate with various reaction times and analyzed using SEM, XPS and XRD. To understand the difference between an initial and a steady-state growth on a quality substrate, the film thickness and growth rate of W_2N film at 680°C as a function of reaction time are shown in Fig. 2. One of the main features in this plot is that it shows a break at about 15 min, which separates higher and lower growth rate regions. The film growth (rate: 122 nm min^{-1}) increased at the initial stage of the reaction whereas the growth (rate: 29 nm min^{-1}) progressed gradually at a steady state. Fig. 3 shows the X-ray diffraction pattern of tungsten nitride films on quartz substrates. From the XRD studies, only β-W_2N was obtained without any diffraction lines indicating WN in the diffractogram. An apparently good relationship between the film thickness and a preferential crystalline plane was observed. The W_2N film prepared at 15 min showed a strong (200) line with an unidentified line. The intensity of the (111) line increased with increasing reaction time and dominated above 15 min, whereas the intensity of the (200) line decreased. The results indicated that W_2N (200) plane was preferably deposited for a relatively less thickness (0.5 μm), but

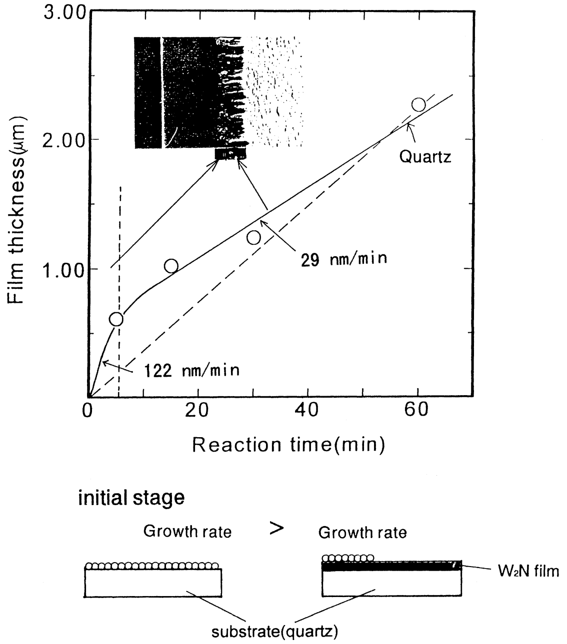


Fig. 2. The film thickness and deposition rate of thin film of tungsten nitride on quartz-glass substrate at 680°C with reaction time.

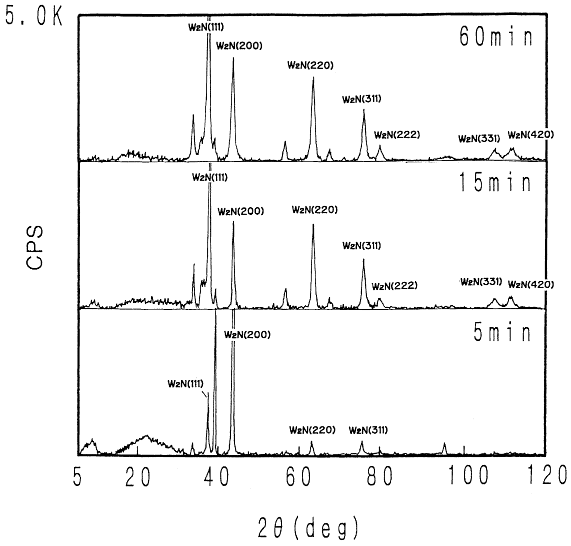
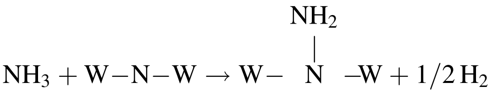


Fig. 3. X-ray diffraction patterns of tungsten nitride thin films deposited on quartz-glass substrate at 680°C and at (a) 5, (b) 15, and (c) 60 min.

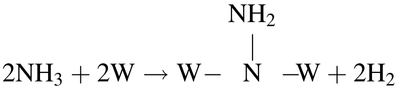
W_2N (111) plane was mainly orientated above thickness of 1 μm. Some small peaks, (220), (311), and (222), were also detected. The half-width of a diffraction line was proportional to the crystallite size of W_2N (200).

Fig. 4 shows the SEM images of tungsten nitride film with reaction time at 680°C. This difference suggested the growth of W_2N on a quartz plate and that on a W_2N crystal film. At 5 min (a), initial stage, 0.1 μm fine particle was formed with a relatively random formation of 0.6 μm thickness (A). The trend of growing particles was observed at reaction time of 15 min as the upper-pillar structure (B) started to form on the film with the structure (A) around 15 min. At 60 min (C), the particles were agglomerated and grew larger, round particles of 0.3∼0.5 μm with 2.6 μm thickness. These SEM images show a good transition of film formation of tungsten nitride from an initial stage to a steady state. Pillar structural films were grown on the fine particle gathered film near the quartz-substrate. At steady state, growth of a pillar-like structural arrangement was observed. Thus, an irregularity on the surface particles of the tungsten nitride film increased with increasing thickness. Therefore, W_2N crystal grew on a quartz plate at an initial stage and was built up on a W_2N film at a steady state. The composition of tungsten nitride from XPS analysis was $W_2N_{1.2}$, $W_2N_{1.0}$, and $W_2N_{0.71}$ at 5, 30, and 60 min, respectively. The film composition increased with reaction time. The film at an initial stage contained more nitrogen than that at the final stage. Dawson and Hansen [10] reported the mechanism of nitrogen addition to tungsten nitride in ammonia synthesis on tungsten as follows:



$$NH_3 + W{-}N{-}W \rightarrow W{-}\overset{\displaystyle NH_2 \atop |}{N}{-}W + 1/2\,H_2$$

and



$$2NH_3 + 2W \rightarrow W{-}\overset{\displaystyle NH_2 \atop |}{N}{-}W + 2H_2$$

This proposed mechanism offers the reason of the presence of a relatively large amount of nitrogen content in tungsten nitrides.

3.2. *Deposition scheme of tungsten nitride on CVD catalyst*

The change in film thickness of tungsten nitride on CVD/alumina catalyst deposited at 700°C as a function of deposition time is shown in Fig. 5. The film thickness of tungsten nitrides gradually increased with increasing deposition time up to 60 min and then rapidly increased, while the BET surface area decreased with deposition time but in turn increased from 60 min, reaching the approximate value of alumina at 120 min. Thus, the BET surface area once decreased and then increased, although the film thickness monotonously increased. The inner and outer surface areas increased with increasing deposition time but pore size volume was not changed during CVD. The SEM images for 30 and 90 min at 700°C were observed for surface morphology in Fig. 6. Tungsten nitride crystal was formed alongside the Al_2O_3 fling at 30 min but at 90 min tungsten nitride film was observed originally. A ribbon-like fold was accumulated on the support.

The micropore distribution of the CVD/alumina catalyst varying with deposition time was analyzed by Dolimore–Heal method in Fig. 7. The approximately 2 and 1.2 nm-micropores on alumina gradually

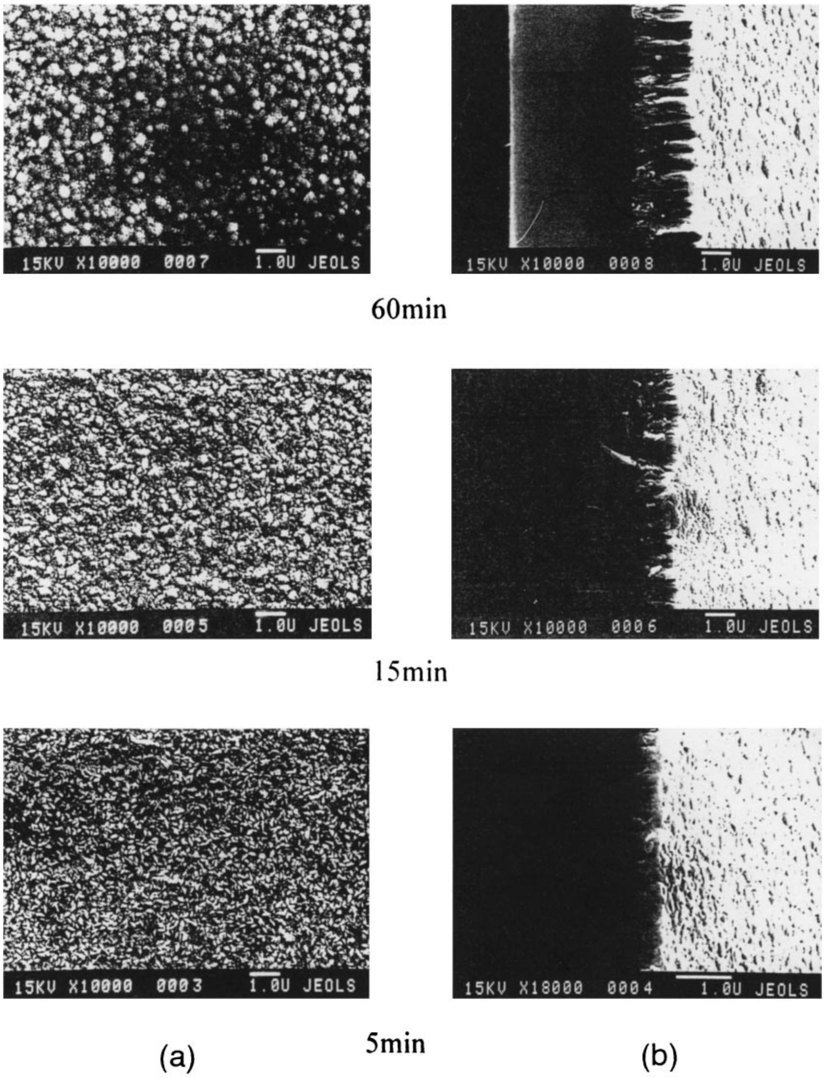


Fig. 4. SEM images of thin films of tungsten nitride on quartz-glass substrate at 680°C with reaction time.

decreased up to 30 min and then 1.2 and 1.0 nm-pore sizes increased with deposition time from 30 to 60 min. Further deposition of W_2N increased 2 nm-micropores and lowered 1.5 nm-micropores. Therefore, the scheme of the deposition of tungsten nitride on alumina at 700°C in the CVD process is shown in Fig. 8. The deposition of tungsten nitride initially plugged the micropores on alumina and then grew on the deposition nitride, increasing the surface area with the growth of tungsten nitride with high surface area micropores on the alumina surface. Furthermore, for the CVD/alumina catalyst, tungsten nitrides on alumina at 90 min deposition time was observed with a small peak of highly crystallite β-W_2N (111) phase.

3.3. XPS of deposited composition

The XPS spectra of W_{4f} and N_{1s} for tungsten nitrides deposited on quartz plate and γ-alumina are shown in Fig. 9(a) and (b). The binding energies of W_{4f} XPS at 32.0 and 34.0 eV were observed for the CVD/alumina catalyst as well as the W_2N crystal on

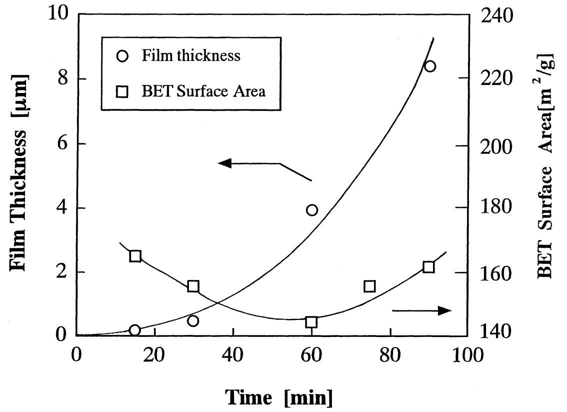


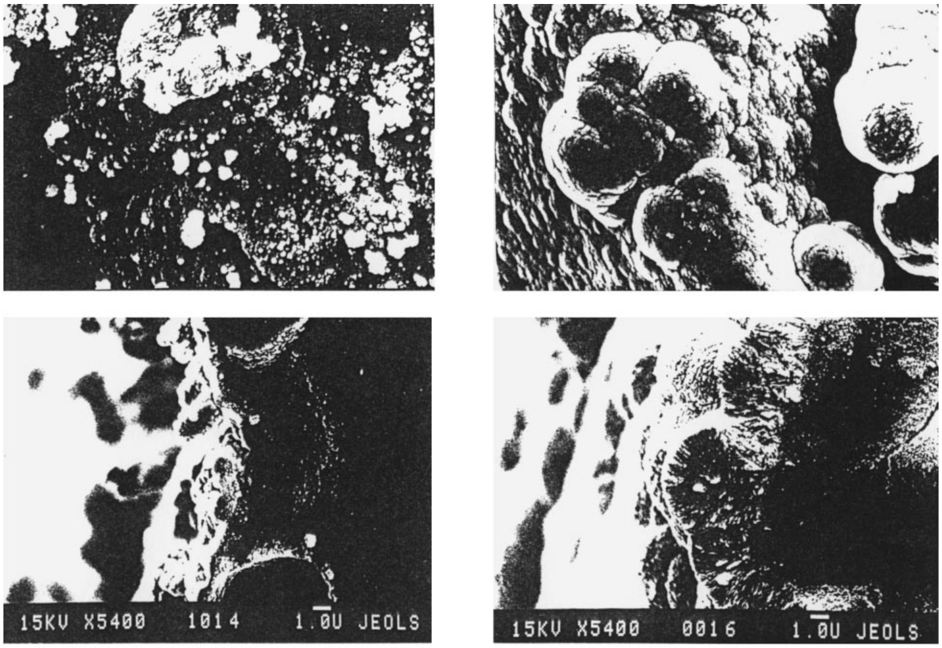
Fig. 5. The change in film thickness and BET surface area of the alumina-supported tungsten nitride catalyst nitrided at 700°C as a function of deposition time.

quartz. This suggested the formation of W_2N crystal on quartz plate. At 15 min the XPS peak of the tungsten nitride was broad showing the interaction of the tungsten nitride with alumina. At 30 min, the peak was similar to that of W_2N powder but in 90 min the peak was in turn similar to W_2N film. Therefore, with time W_2N was first interacted with alumina as W_2N powder was accumulated and then W_2N film was formed on alumina.

The N_{1s} spectra showed a main peak at 397.2 eV with a shoulder peak at 399.2 eV. The lower binding energy feather at 397.2 eV is characteristic of a W–N bonding (nitride). The N_{1s} binding energy was reported to be 397.0 eV for a W_2N film [2,4], 397.6 eV for a VNx [11], and 397.3 eV for a NbN film [11] made by CVD. The peak at 397.2 eV was attributed to $N^{\delta-}$, similar to the nitride ion. The peak at 399.2 eV was ascribed to the nitrogen atom or molecule present in the interstitial sites of tungsten nitrides. Furthermore, the XPS analysis shows no Cl^- ions on the surface of the catalysts after the CVD deposition although WCl_6 was used as a feed.

3.4. *Effect of supports*

In order to determine the effect of the supports such as alumina, quartz sand, and zeolite Y on the deposition of tungsten nitride during CVD, the BET surface



(a) 30min CVD Preparation (b) 90min CVD Preparation

Fig. 6. SEM images of thin films of the alumina-supported tungsten nitride deposited at 700°C in (a) 30, and (b) 90 min.

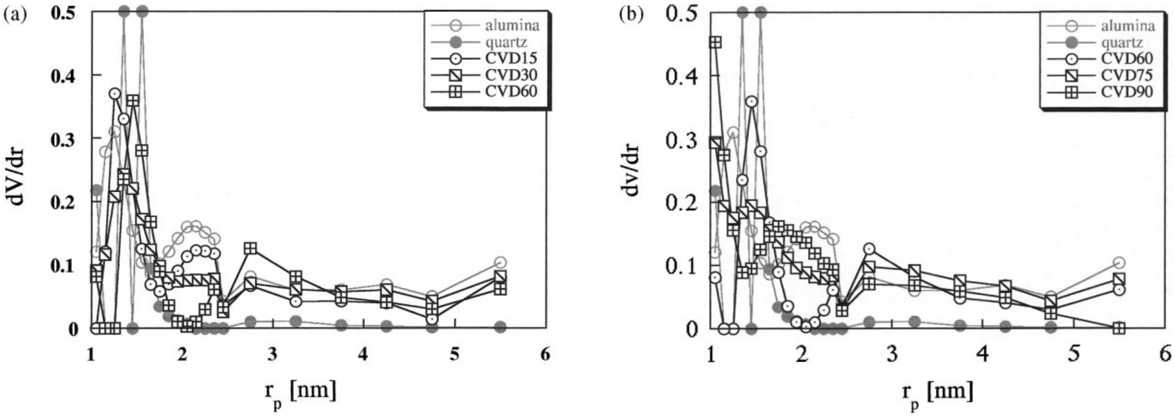


Fig. 7. Pore size distribution of the alumina-supported tungsten nitride with deposition time.

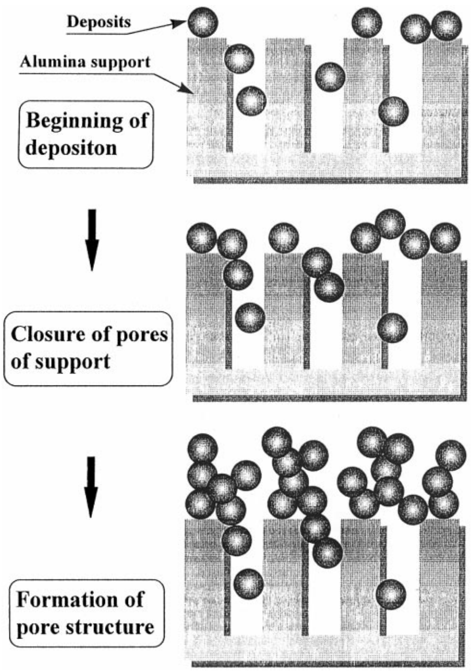


Fig. 8. The scheme of the deposition of tungsten nitride on alumina.

areas of the catalysts before and after CVD are shown in Fig. 10. When quartz sand and γ-Al_2O_3 were used as a support, the surface areas were hardly changed before and after CVD deposition, while for zeolite Y the BET surface area increased by 15% after CVD. From the result, tungsten nitride with large surface area grew to form on zeolite Y with large surface area. The surface area of the CVD catalysts depended on that of all the supports, suggesting that the surface layer of deposited compounds was controlled by the micropore structure of the supports as well as micropores of W_2N itself.

3.5. *HDS of thiophene*

Fig. 11 shows the activities of the CVD/alumina for the HDS of thiophene at 300°C and atmospheric pressure. The CVD/alumina catalysts deposited for 15 and 30 min showed a constant activity during the reaction and the latter catalyst was twice as active as the former one. The activity of the catalyst deposited at 90 min, however, decreased with increasing reaction time up to 160 min and in turn increased with reaction time. From the result, tungsten nitride in the catalyst deposited at 90 min was similar to a bulk with tungsten loadings of 50%. The tungsten nitride was reduced and activated for 160 min. This result suggested that different kinds of tungsten nitride of the CVD/alumina catalyst were generated to activate as discussed before. From the XPS analysis, the W_{4f} peaks of the deposited tungsten nitride were shifted to lower binding energies and the N_{1s} peaks were shifted to a lower position at higher deposition temperature. It is likely that electron transfer occurs from tungsten to the nitrogen atom, and therefore, tungsten was more reduced and active in thiophene HDS. With time, W_2N was first interacted with

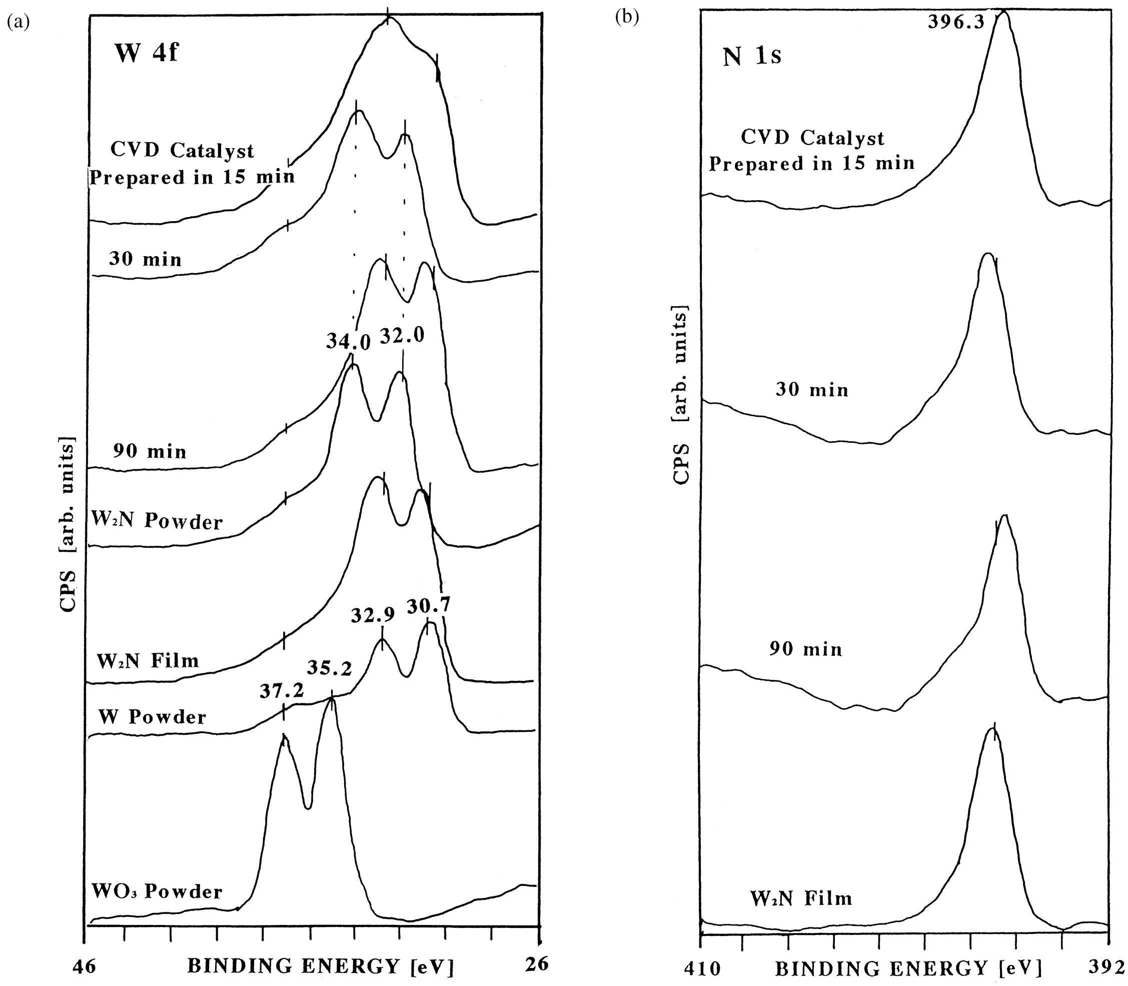


Fig. 9. XPS (a) W_{4f} and (b) N_{1s} spectra of the tungsten nitride catalyst deposited on quartz sand and γ-alumina.

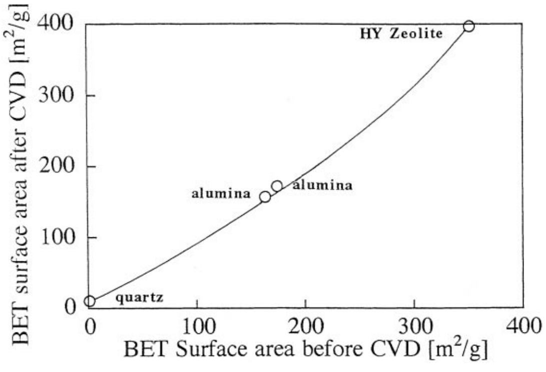


Fig. 10. The BET surface area of the tungsten nitrides catalyst on the supports before and after CVD deposition.

alumina as W_2N powder was accumulated and then W_2N film was formed on alumina. The surface area of the CVD catalysts depended on that of all the supports suggesting that the surface layer of deposited compounds was controlled by the micropore structure of the supports as well as micropores of W_2N itself.

After the reaction, the CVD/alumina catalyst deposited at 700°C in 90 min was analyzed using the XPS measurement to determine whether or not tungsten sulfide was formed during reaction. No XPS S 2p spectra were observed for the spent catalyst, supporting the fact that the catalyst was not sulfided during the reaction.

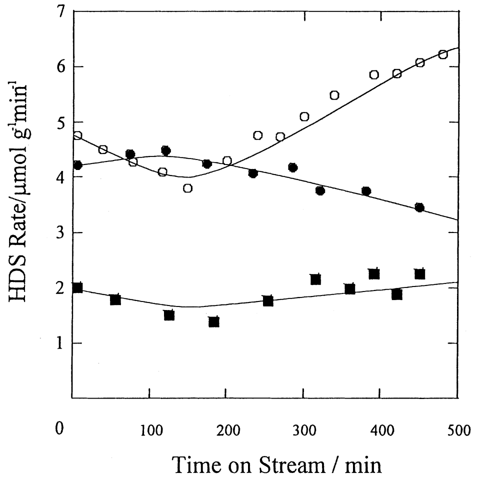


Fig. 11. The HDS of thiophene on the alumina-supported CVD catalyst deposited at 700°C in (■) 15, (●) 60, and (○) 90 min at reaction temperature of 300°C.

4. Conclusions

A thin film of tungsten nitride was deposited on quartz substrate and γ-alumina by the reaction of WCl_6 with NH_3, H_2, and Ar gases at 700°C under reduced pressure. A dense, uniform and lustrous film was formed. β-W_2N was formed without any diffraction line of WN. The γ-alumina-supported tungsten nitride catalyst with 161 m^2 g^{-1} surface area was prepared by the CVD method in a stream of WCl_6, NH_3, H_2, and Ar gases at 700°C and 70 Pa. The deposition of tungsten nitride initially plugged the micropores on alumina and then grew on the deposition nitride increasing the surface area with the growth of tungsten nitride, with high surface area micropores on the alumina surface. The activities of the CVD/alumina in the HDS of thiophene was determined at 300°C and atmospheric pressure.

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