Preparation of highly active NiW hydrotreating model catalysts with 1,2-cyclohexanediamine-*N*,*N*,*N*′*N*′-tetraacetic acid (CyDTA) as a chelating agent

G. Kishan, L. Coulier, V. H. J. de Beer, J. A. R. van Veen and J. W. Niemantsverdriet*

Schuit Institute of Catalysis, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands.
E-mail: j.w.niemantsverdriet@tue.nl

Received (in Oxford, UK) 25th April 2000, Accepted 16th May 2000
Published on the Web 8th June 2000

Changing the order in which oxidic W and Ni convert to sulfides by adding 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) as a chelating agent for nickel in the preparation of NiWS–SiO_2 catalysts is the key ingredient in obtaining a high activity for thiophene hydrodesulfurization.

Stringent future legislation for low-sulfur diesel fuel places increasingly higher demands on the performance of hydrotreating catalysts.[1,2] Supported sulfides of molybdenum or tungsten promoted with nickel or cobalt are widely applied to this end.[2] In the preparation, sulfidation of the oxidic precursors in a mixture of H_2S–H_2 or in the sulfur-containing hydrocarbon feed is an essential step. The sulfidation of supported MoO_3 and oxidic CoMo and NiMo catalysts has received considerable attention.[3–10] The generally accepted view is that in order to obtain active CoMoS and NiMoS catalysts, sulfidation of molybdenum should precede that of cobalt and nickel, such that the reactive edges of the MoS_2 slabs can serve as anchoring sites for the promoter atoms.[8–10] Chelating agents such as nitrilotriacetic acid (NTA)[9,10] and ethylenediaminetetraacetic acid (EDTA)[4,5] assist in stabilizing nickel and cobalt, such that their conversion to sulfides is retarded with respect to molybdenum.

Much less is known about tungsten sulfidation. Tungsten oxide is more difficult to convert to sulfides than molybdenum.[3,11] Shimizu *et al.*[12] report that chelating agents improve the activity of NiW–Al_2O_3 catalysts in hydrodesulfurization of benzothiophene and hydrogenation of *o*-xylene. The origin of the promotional effect is not clear, however.

Our purpose is to demonstrate that addition of 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) as a chelating agent for Ni in the preparation of NiWS–SiO_2 catalysts leads to a 2.3-fold increase in thiophene hydrodesulfurization activity, as compared to a standard NiWS–SiO_2 catalyst. We correlate the catalytic activity with the order in which nickel and tungsten convert to sulfides, as measured by X-ray photoelectron spectroscopy (XPS). To measure XPS spectra at improved resolution, we used model supports consisting of a thin hydrophilic SiO_2 layer on a silicon substrate.[13]

SiO_2 supports were prepared by oxidizing Si(100) at 750 °C for 24 h in air. Oxidized wafers were cleaned in H_2O_2–NH_3(aq) (3 : 2 v/v) at 65 °C and hydroxylated in boiling water for 30 min. The sample was covered with an aqueous solution of ammonium metatungstate (Merck), nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$; Merck] and 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid ($C_{14}H_{22}N_2O_8 \cdot H_2O$; Merck) and spin coated under N_2 at 2800 rpm.[14] Concentrations were adjusted to result in loadings of 6 W atoms nm^{-2} and variable Ni loading between 1 and 6 atoms nm^{-2}. The amount of CyDTA added was equal to the amount of Ni present. Catalysts prepared without CyDTA were calcined (500 °C, 30 min), whereas NiW-CyDTA–SiO_2 catalysts were used without calcination. Sulfidation was carried out in a glass tube reactor with 10% H_2S in H_2 at a heating rate of 5 °C min^{-1} (2 °C min^{-1} for NiW-CyDTA–SiO_2) to the desired temperature, after which samples were kept at that temperature for 30 min. Next, the sample was cooled to room temperature under helium and transported to the XPS under N_2 atmosphere.

XPS spectra were obtained on a VG Escalab 200MK spectrometer, at a constant pass energy of 20 eV. Binding energies were corrected with reference to the Si 2p peak of SiO_2 at 103.3 eV.

Thiophene hydrodesulfurization was carried out with 5 cm^2 of model catalyst in a microflow reactor operating in batch mode (1.5 bar, 400 °C, with 4% thiophene in H_2), after sulfidation at 400 °C. Gas samples were taken with a syringe for gas chromatograph (GC) analysis of the products. All activity results presented are the average of at least six different measurements, which showed good reproducibility.

Fig. 1 shows W 4f and Ni 2p XPS spectra of the NiW-CyDTA–SiO_2 model catalyst after sulfidation at the indicated temperatures. The W 4f spectrum of the fresh catalyst shows a doublet at 35.6 eV characteristic of W(VI) oxide.[15] The small peak at 41.6 eV corresponds to the W $5p_{3/2}$ state. As Fig. 1 shows, sulfidation of W starts at 150 °C and is completed at 300 °C, where the W 4f spectrum shows a doublet at 32.6 eV, characteristic of WS_2.[15] Sulfidation of a Ni-free W–SiO_2 sample (not shown) proceeded similarly to the progression shown in Fig. 1A. Addition of CyDTA to W–SiO_2 in the preparation had no measurable effect on the sulfidation rate of tungsten.

Sulfidation of Ni, however, is greatly affected by CyDTA. The Ni 2p spectrum of fresh NiW-CyDTA–SiO_2 (Fig. 1B) exhibits the pattern characteristic of Ni^{2+}, with the Ni $2p_{3/2}$ peak at 855.4 eV accompanied by shake-up features.[15] The Ni $2p_{3/2}$ binding energy, however, is 1.5 eV lower than that of Ni in CyDTA-free Ni–SiO_2 and NiW–SiO_2 catalysts, evidencing complexation of nickel by CyDTA. As Fig. 1B shows, the complexed nickel is stable in H_2S–H_2 upto temperatures just below 250 °C. In contrast, NiO reacts in H_2S at room temperature, and conversion to nickel sulfide (Ni $2p_{3/2}$ binding energy of 854.0 eV[15]) is complete at 100 °C. The same is true for Ni sulfidation in NiW–SiO_2 catalysts, however, the Ni $2p_{3/2}$ peak shifts to a higher binding energy of 854.5 eV after complete sulfidation of W at sulfidation temperatures around 300 °C. We take the additional 0.5 eV shift of the Ni $2p_{3/2}$ peak as evidence that the initially formed Ni_3S_2 rearranges, and redisperses over the reactive edges of the WS_2 slabs, as proposed by Reinhoudt *et al.*[11]

Fig. 1B shows that CyDTA retards the sulfidation of Ni to *ca.* 250–300 °C. This temperature range coincides with the disappearance of the N 1s signal characteristic of the CyDTA ligand, indicating that the decomposition of the latter determines the rate of Ni sulfidation.

The activity of the catalysts for thiophene hydrodesulfurization is shown in Fig. 2. The blank silica support in the reactor has an order of magnitude lower activity than W–SiO_2, and shows mainly cracking products. The W–SiO_2 catalyst calcined at 500 °C is detectably active, with a product distribution showing predominantly 1-butene as the primary product. The Ni–SiO_2 catalyst calcined at 500 °C exhibits lower activity. Synergism is clearly observed in the standard NiW–SiO_2 model

DOI: 10.1039/b003272g

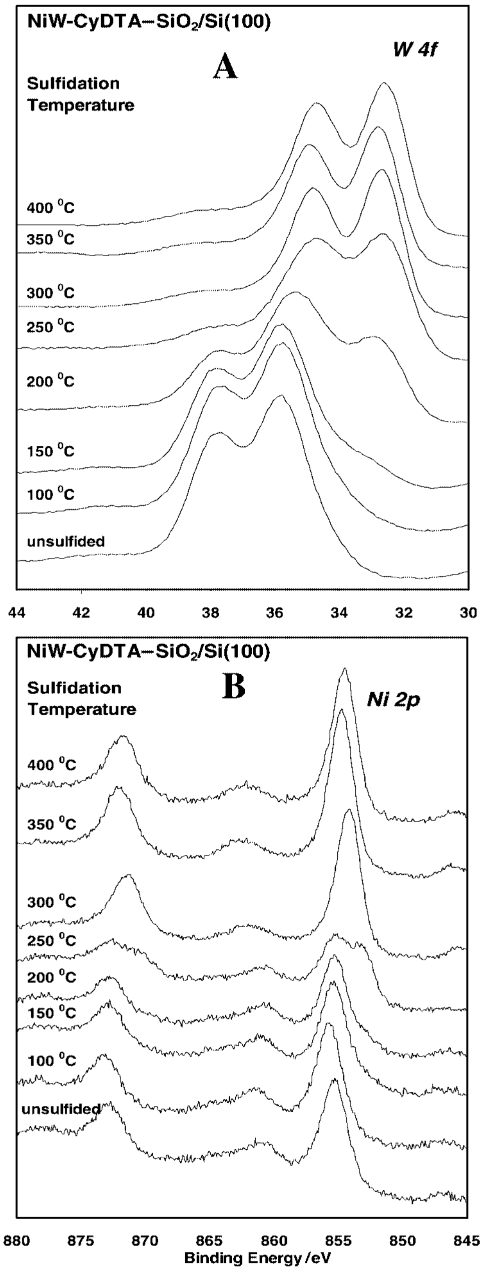

Fig. 1 (A) W 4f and (B) Ni 2p XP spectra of NiW-CyDTA–SiO_2/Si(100) model catalysts during sulfidation at various temperatures. The spectra show that CyDTA retards the sulfidation of Ni such that the sulfidation of W precedes that of Ni.

catalyst, for which the total activity is more than twice that of Ni–SiO_2 and W–SiO_2 combined. The highest activity is observed with NiW-CyDTA–SiO_2, which is about 2.3 times more active than a standard NiW–SiO_2 sample of the same nominal composition. The C_4-product distribution of this catalyst is: 40% 1-butene, 36% *trans*-2-butene and 24% *cis*-2-butene. Optimum activity was observed with NiW–SiO_2 catalysts containing 4 Ni atoms or more, in addition to 6 W atoms nm^{-2} on SiO_2. This level of conversion corresponds to a pseudo-turnover frequency of 4×10^{-2} mol (thiophene) mol(W + Ni)$^{-1}$ s^{-1}. Increasing the Ni loading further did not influence the activity significantly. Interestingly, the optimum Ni/W atomic ratio of 0.66 equals that in commercial NiW–Al_2O_3 catalysts.[2]

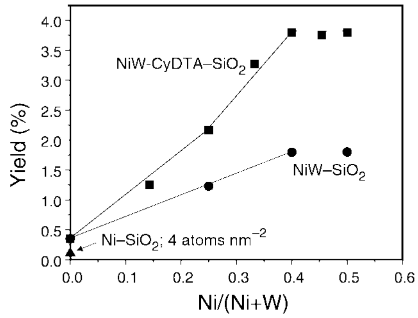

Fig. 2 Thiophene HDS activity as a function of Ni-content in NiWS–SiO_2/Si(100) model catalysts containing 6 W atoms nm^{-2} (batch reaction at 400 °C, runtime 1 h).

We attribute the high HDS activity of NiW-CyDTA–SiO_2 to the retardation of nickel sulfidation by the chelating agent to temperatures where WS_2 has already formed. As a result, Ni atoms released by CyDTA can move to the edges of WS_2 to form a finely dispersed NiW sulfide. A similar phase, commonly referred to as CoMoS, has been identified as the active phase in sulfided CoMo catalysts by Topsøe and coworkers.[2] A similar structure may be invoked to explain the high activity of sulfided NiW catalysts. The reason that standard NiW–SiO_2, in which Ni-sulfidation is not retarded by complexing agents, shows appreciable promotion of desulfurization activity is that the Ni_3S_2 phase which forms at low temperatures redisperses at higher temperatures and may still end up in the form of suboptimal clusters on the edges of WS_2, as recently proposed by Reinhoudt *et al.*[11] However, application of sufficiently stable chelating agents such as CyDTA, that retard Ni sulfide formation to temperatures where WS_2 has formed, results in the most active form of the NiWS catalyst, as demonstrated in this paper.

Notes and references

1 J. W. Gosselink, *CatTech.*, 1998, **4**, 127.
2 H. Topsøe, B. S. Clausen and F. E. Massoth, *Hydrotreating Catalysis*, Springer-Verlag, Berlin, 1996.
3 B. Scheffer, P. J. Mangnus and J. A. Moulijn, *J. Catal.*, 1990, **121**, 18.
4 L. Medici and R. Prins, *J. Catal.*, 1996, **163**, 38.
5 R. Cattaneo, T. Shido and R. Prins, *J. Catal.*, 1999, **185**, 199.
6 A. M. de Jong, H. J. Borg, L. J. van IJzendoorn, V. G. M. F. Soudant, V. H. J. de Beer, J. A. R. van Veen and J. W Niemantsverdriet, *J. Phys. Chem.*, 1993, **97**, 6477.
7 Th. Weber, J. C. Muijsers, J. H. M. C. van Wolput, C. P. J. Verhagen and J. W. Niemantsverdriet, *J. Phys. Chem.*, 1996, **100**, 14 144.
8 L. Coulier, V. H. J. de Beer, J. A. R. van Veen and J. W. Niemantsverdriet, *Top. Catal.*, 2000, in press.
9 J. A. R. van Veen, E. Gerkema, A. M. van der Kraan and A. Knoester, *J. Chem. Soc., Chem. Commun.*, 1987, 1684.
10 A. M. de Jong, V. H. J. de Beer, J. A. R. van Veen and J. W Niemantsverdriet, *J. Phys. Chem.*, 1996, **100**, 17 722.
11 H. R. Reinhoudt, Y. van der Meer, A. M. van der Kraan, A. D. van Langeveld and J. A. Moulijn, *Fuel. Process. Technol.*, 1999, **61**, 43.
12 T. Shimizu, K. Hiroshima, T. Honma, T. Mochizuki and M. Yamada, *Catal. Today*, 1998, **45**, 271.
13 P. L. J. Gunter, J. W. Niemantsverdriet, F. H. Ribeiro and G. A. Somorjai, *Catal. Rev.-Sci. Eng.*, 1997, **39**, 77.
14 R. M. van Hardeveld, P. L. J. Gunter, L. J. van IJzendoorn, W. Wieldraaijer, E. W. Kuipers and J. W. Niemantsverdriet, *Appl. Surf. Sci.*, 1995, **84**, 339.
15 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of XPS*, Perkin-Elmer Corporation, Eden Prairie, MN, 1992.