Periodic Trends in the Hydrodenitrogenation Activity of Carbon-Supported Transition Metal Sulfide Catalysts

Periodic trends of transition metals for the catalysis of reactions such as hydrogenation, hydrogenolysis, isomerization and hydrocarbon oxidation have been well studied (*1*). When activity versus position of the transition metal in the periodic table is plotted, quite often these trends are manifested in the form of so-called volcano-type curves. Recently, the periodic trends of unsupported group V, VI, VII and VIII transition metal sulfides for the catalysis of the hydrodesulfurization (HDS) of dibenzothiophene at moderately high pressure (30 bar) were presented by Pecoraro and Chianelli (*2*). In subsequent studies (*3–5*) correlations were made between the sulfides' heats of formation and electronic structures on the one hand, and their catalytic activities for HDS on the other. A similar study on the HDS of thiophene at atmospheric pressure has been carried out by Vissers *et al.* (*6*). In that study, carbon-supported transition-metal sulfide catalysts were used instead of the unsupported systems studied by Pecoraro and Chianelli (*2*). Just as for the unsupported systems tested with dibenzothiophene, volcano-type curves were observed for the carbon-supported second- and third-row transition-metal sulfides tested with thiophene. In the supported systems the maxima were positioned at Rh an Ir, while in the unsupported systems they were located at Ru and Os. Very recently, another study on the HDS of thiophene at atmospheric pressure and catalyzed by carbon-supported transition metal sulfides was published by Ledoux *et al.* (*7*). The results of their activity measurements of all available transition-metal sulfides (groups I–VIII) compare very well with those obtained by Vissers *et al.* (*6*). The results of these three studies (*2, 6,*

7) are in good agreement: similar volcano curves for the second- and third-row transition metal sulfides and a double-maximum curve for the first-row transition metal sulfides. This is not really surprising because the reactions studied are basically of the same type. The only differences are in the reaction pressure and molecular size of the model compounds, and the reaction mechanism is the same, with ring opening and hydrogenolysis preceding the (ring-) hydrogenation. Also, since the transition metal sulfides interact weakly with the carbon support, not much difference between unsupported and carbon-supported catalysts is to be expected. However, the behavior of these catalytic systems may very well be different when another reaction mechanism is involved, as in the case of the hydrodenitrogenation (HDN) reaction, in which ring hydrogenation always precedes ring opening and hydrogenolysis (*8*).

In the present study, we have chosen the HDN of quinoline at moderately high pressure as a model reaction, and we have used the same carbon-supported transition metal sulfide catalysts studied by Vissers *et al.* (*6*). They were prepared by pore volume impregnation of the support (activated carbon Norit RX3 extra: surface area, 1190 $m^2\ g^{-1}$; pore volume, 1.03 $cm^3\ g^{-1}$) with aqueous solutions of group V, VI, VII, and VIII transition metal salts and drying in air at 383 K. The surface loading was approximately 0.5 metal atoms nm^{-2}. The catalytic reaction was carried out in a stirred micro-autoclave (*9*) (volume, 20 cm^3) equipped with an inlet and outlet system and a manometer. The inlet system consists of an inlet tube (down to about 1 cm from the bottom of the autoclave) connected with a

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2.5-cm³ storage vessel (liquid reactant mix-ture) which in turn is connected with two separate gas supply lines for H_2 and for an H_2S/H_2 gas mixture. This inlet system was used for the introduction of the sulfiding gas mixture and the liquid reactant and for pressurizing the autoclave with H_2. The procedure applied for the activity test was as follows: First, a 25-mg sample of the dried catalyst was introduced and the auto-clave was assembled. Subsequently, the catalyst was sulfided *in situ* with a mixture of 10% H_2S in H_2 (Air Products, $H_2 >$ 99.9995%, $H_2S > 99.9$%) at a flow rate of 60 cm³ min⁻¹ and the following temperature program was applied: linear increase (6 K min⁻¹) from 293 to 653 K and 1 h at 653 K. On the basis of earlier findings (6) we assumed that under these conditions the catalysts are fully sulfided. After sulfidation the catalyst was left in the H_2S/H_2 atmo-sphere and was cooled to room tempera-ture. Then the liquid storage vessel was filled with 2 cm³ of the reactant mixture consisting of 93.6 mol% hexadecane (Jans-sen Chimica, >99%), 5.9 mol% quinoline (Janssen Chimica, >99%), and 0.5 mol% CS_2 (Janssen Chimica, >99.5%), the vessel was pressurized with H_2 (Hoekloos, >99.9%), and the liquid was injected into the autoclave. It is only at this stage of the experimental procedure that a small amount of air enters the autoclave. How-ever, the presence of CS_2 in the reaction mixture ensures that the catalyst remains sulfided during the reaction. After the reac-tant mixture was introduced the pressure in the autoclave was adjusted to the desired value (40 bar). The stirring was started and the temperature was increased slowly to 653 K (6 K min⁻¹) and held at 653 K for 3 h. The reaction pressure was approximately 50 bar. After the reaction was completed the autoclave was cooled rapidly (20 min) and the liquid was removed from the auto-clave. The liquid was analyzed with a Hewlett–Packard 5890A gas chromato-graph with a 50-m capillary CP Sil-5 column (Chrompack) with temperature program-

ming and an FID detector. The follow-ing reaction products and intermediates were identified: hydrocarbon products (propylcyclohexane, propylcyclohexene, propylbenzene), N-containing intermedi-ates (decahydroquinoline, 1,2,3,4-tetrahy-droquinoline, 5,6,7,8-tetrahydroquinoline, orthopropylaniline), and unconverted quin-oline. The conversion was defined as (hy-drocarbon products × 100)/(unconverted quinoline + N-containing intermediates + hydrocarbon products). The complete ex-perimental set-up consists of three identical autoclaves operated simultaneously. In this way the activity of each catalyst can easily be measured in triplicate to compensate for fluctuations. The standard deviation was 10% or less.

The results of these short activity tests are shown in Fig. 1. The activities of the first-row transition-metal sulfides are quite low, comparable to that of an autoclave filled with carbon support only. No maxi-mum was found for Cr sulfide nor for Co sulfide. The lower activity of these two sulfides contrasts to their good HDS activi-ties as measured by Vissers et al. (6) (Fig. 2). The low HDN activity observed for all first-row transition metal sulfides is prob-ably due to their lower hydrogenation
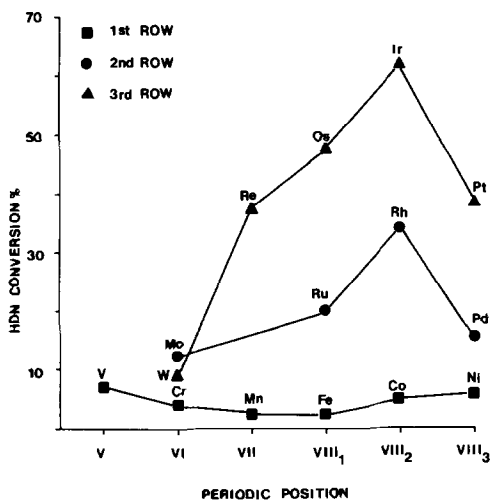

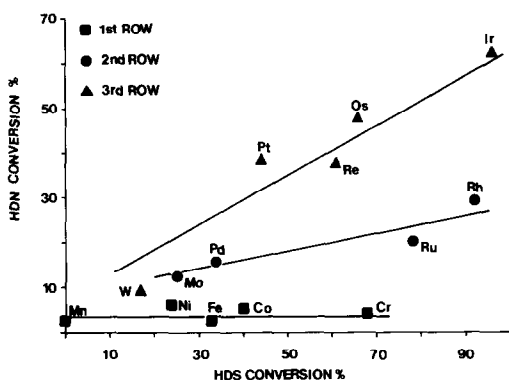
FIG. 1. Periodic trends for HDN of quinoline.

FIG. 2. Correlation between HDN of quinoline (653 K, 50 bar) and HDS of thiophene (673 K, 1 bar) (6).

activity. The second-row transition metal sulfides are more active than those of the first row, with an exception of Mo sulfide. The other three metal sulfides (Ru, Rh, and Pd) have higher activities, with a maximum at Rh. The position of this maximum is consistent with the results of Vissers et al. (6) and Ledoux et al. (7) in the HDS of thiophene. The highest activities were found for the third-row transition metal sulfides. Only W sulfide had a very low activity, comparable to that of Mo sulfide and those of the first-row metal sulfides. The activities of the other four metal sulfides (Re, Os, Ir, and Pt) were almost twice as high as those of the sulfides of the second row. These results differ from those of the HDS studies (2, 6, 7), in which almost no difference was found between the activities of the second- and the third-row transition metal sulfides. The maximum activity in the third-row transition metal sulfides for HDN was found for Ir sulfide. This maximum is also consistent with the results of the HDS studies of Vissers et al. (6) and Ledoux et al. (7).

The results of these quinoline HDN experiments demonstrate the importance of the metal sulfide in hydrotreatment. The metal sulfides themselves can catalyze the different steps of hydrotreatment: ring hydrogenation, ring opening, and hydrogenolysis. Since carbon that we used is a rather inert support, the properties of the metal sulfides themselves determine the activities and selectivities of the carbon-supported catalysts, and these properties are a function of the position of the metal in the periodic table. Apparently the role of the support in HDN is less important than has been anticipated up to now. The low activities of the first-row transition metal sulfides, Mo sulfide, and W sulfide have increased our curiosity for an explanation of the promoter effect in hydrotreatment, since from other experiments we have learned that the combination of the low-activity Ni and Mo sulfides on carbon support gives an outstanding HDN and HDS catalyst.

A comparison of our HDN experiments with the HDS results of Pecoraro and Chianelli (2), Vissers et al. (6), and Ledoux et al. (7) shows differences as well as agreements. An explanation of these facts will not be possible without additional studies on the separated catalytic functions of these carbon-supported metal sulfides. The present study will therefore be continued using the HDN of decahydroquinoline and the hydrogenation of biphenyl as test reactions in order to separate the hydrogenolysis and ring-opening steps from the ring hydrogenation step. In this way we expect to further the understanding of the industrially important HDN reaction.

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