Journal of Catalysis **189,** 209–220 (2000)
Article ID jcat.1999.2696, available online at http://www.idealibrary.com on

# Zeolite Y-Supported Cobalt Sulfide Hydrotreating Catalysts

## III. Prevention of Protolysis and the Effect of Protons on the HDS Activity

M. J. Vissenberg,* P. W. de Bont,† W. Gruijters,* V. H. J. de Beer,* A. M. van der Kraan,†
R. A. van Santen,* and J. A. R. van Veen*

**Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; and †Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands*

Received July 12, 1999; revised September 14, 1999; accepted September 28, 1999

**Zeolite Y-supported Co sulfide catalysts were prepared by using different supports (NaY or CaY) and precursors ($CoCl_2$ or $Co(CO)_3NO$) to prevent the negative effect on the thiophene HDS activity caused by protolysis. It appeared that protolysis could be retarded by partially blocking the sodalite cages with $Ca^{2+}$ cations. The catalysts were prepared via gas phase adsorption (Co(GPA)NaY) and via ion exchange (CoNaY and CoCaY). They differ in amount of protons after sulfidation, which make the study of synergetic effect of protons on the thiophene HDS activity possible. It turned out that in zeolite-supported metal sulfides (Co or Ni) prepared by ion exchange an interaction exists between protons and the metal sulfide, resulting in a high dispersion and consequently a high activity. However, the industrial applications of this type of catalysts may be limited because bases like $NH_3$ and $H_2O$ disturb the metal sulfide–proton interaction, resulting in loss of dispersion. The synergetic effect between protons and metal sulfide cannot be explained only by an improvement of dispersion. Possibly, the protons themselves play an active role in the HDS reaction or act as a structural promoter by, e.g., increasing the electron deficient character of the metal sulfide.** © 2000 Academic Press

*Key Words:* **hydrodesulfurization; acidity; metal sulfides; thiophene; zeolites.**

## INTRODUCTION

Zeolites offer the opportunity to prepare well-defined bifunctional catalysts. This makes zeolites an interesting support material to study this kind of catalysts on a fundamental basis. For example, sulfided NiW/ASA (amorphous silica alumina) catalysts are used in single-stage hydrocracking (1) processes. The function of the sulfide is (de-) hydrogenation, which is also necessary for hydrotreating reactions like the removal of sulfur compounds in HDS. The acidity derived from protons of the ASA provides a cracking function. However, the protons may also affect the properties of the metal sulfide and the activity in hydrotreating reactions. Some intriguing results correlated with the presence of protons were found (2, 3) by using zeolite-supported metal sulfides.

The first interesting observation is that protons affect the activity (2). The catalytic properties of zeolite-supported transition metal sulfides (TMS) are often tested in thiophene HDS. It is often concluded, by comparing catalysts at steady-state activities, that the presence of Brønsted acidity has a negative effect on the thiophene HDS activity due to coke formation on the acid sites, resulting in shielding of the metal sulfide (4–6). The coke formation will be less in industrial processes due to a higher $H_2$ pressure. Interestingly, by comparing intrinsic activities (so with only a very small amount of coke formed), it was shown that Brønsted acidity improved the thiophene HDS activity (2, 7). In addition, it was shown that the activity increase of HNaY supported Ni or Mo sulfide with increasing acidity was much stronger than that for HNaY itself (2). Several possibilities for this synergetic effect were suggested (2). These explanations of the function of protons range from the provision of a thiophene adsorption reservoir, an active role in the HDS reaction to a change of the catalytic properties of the metal sulfide in the zeolite pores. Breysse *et al.* (8) studied the hydrogenation of zeolite-supported Ru sulfide. It was shown by IR of adsorbed CO that a higher acidity resulted in a more electron-deficient character of the sulfide particles. The increased electron-deficient character resulted in an increase in hydrogenation activity. The electron deficiency of the Ru sulfide particles was ascribed to an electron transfer from the Ru sulfide to the protons. Mojet (9) showed for supported noble metal catalysts that an electron transfer is not necessary to explain an effect of the support on the electronic structure of the metal particles. The effect could be explained by a model for the metal–support interaction, which is based upon a direct influence of the Madelung potential of the oxide support on the electronic structure of the metal particles. The Madelung potential is a result of electrostatic interactions in an oxide lattice and is determined by all elements in the material. In this way differences in type of cations present in the support will affect the electronic structure of the metal particles. One wonders whether this will be the case for sulfide clusters as well.

0021-9517/00 $35.00

Zhang *et al.* (10) showed that an interaction between zeolite protons and Pd in H-ZSM5 was broken after ammonia treatment, resulting in the migration of Pd to the external surface. This experiment suggests that protons act as an anchor for metals in the zeolite.

A second fascinating observation is the reactivity of the protons with the metal sulfide (3). The sulfidation of CoNaY prepared by ion exchange was studied extensively (3, 11–13). It was observed that up to a sulfidation temperature of 573 K small Co sulfide particles were formed in the supercages, causing a high thiophene HDS activity. These small Co sulfide particles were not stable (not even in 10% $H_2S/H_2$) above 573 K and the thiophene HDS activity strongly decreased with sulfidation temperatures above this temperature. The instability is most probably caused by a protolysis reaction of the charge compensating NaY protons (formed during sulfidation of $Co^{2+}$), resulting in the formation of $H_2S$ and blue colored Co species. These blue Co species are clearly different from the purple $Co^{2+}$ ions in dehydrated CoNaY. The blue colored Co species are most probably located in the hexagonal prisms/sodalite cages, strongly interacting with the zeolite lattice where they are tetrahedrally coordinated by oxygen and/or sulfur (blue color is not caused by sulfur radicals).

The present study can be divided into two parts. First, attention was paid to prevention of the protolysis reaction. Possibly, blocking the sites in the hexagonal prisms/sodalite cages can prevent the formation of the blue colored Co species during protolysis. It is known (14) that $Ca^{2+}$ ions occupy preferentially sites in the hexagonal prisms and/or sodalite cages after dehydration. Therefore, CaY was used as support for Co sulfide. Another possible way of preventing the protolysis reaction is using a precursor, which results in a nonacidic zeolite after sulfidation. Gas phase adsorption of $Co(CO)_3NO$ was applied to obtain this (15, 16). The different catalysts were tested in thiophene HDS after sulfidation at various temperatures (473–773 K) and characterized by transmission electron microscopy (TEM), temperature programmed techniques, and chemical analysis. The second part of the study deals with the role of the protons in relation to the activity. The thiophene HDS activity of zeolite-supported Co sulfide with different amounts of Brønsted acid sites was measured. In addition, the possibility of a $H^+$–TMS interaction, like the $H^+$–metal interaction in PdY (10), was studied by treatment with a base (ammonia and water) after sulfidation of CoNaY and NiNaY followed by measuring the thiophene HDS activity. TEM was used to determine the effect of these treatments on the distribution of the metal sulfides.

## EXPERIMENTAL

### *Preparation and Sulfidation*

NaY (AKZO, $Na_{55}(AlO_2)_{55}(SiO_2)_{137}$, containing 25 wt% physisorbed water) and CaY were used as support. CaY was prepared by ion exchange of NaY with a 0.2 M aqueous solution of $CaCl_2$ followed by washing until $Cl^-$ free (checked with $Ag(NO_3)_2$) and overnight drying at 383 K. This procedure was done twice and resulted in the following unit cell composition: $Ca_{24}Na_7(AlO_2)_{55}(SiO_2)_{137}$ (determined by AAS). Co(Ni)NaY was prepared by ion exchange of 10 g NaY with 250 ml 0.02 M aqueous solution of $Co(Ni)Cl_2$. CoCaY was prepared by ion exchange of 10 g CaY with 250 ml 1 M aqueous solution of $CoCl_2$. After 24 h stirring at room temperature, the Co(Ni)NaY and CoCaY were washed until $Cl^-$ free (checked with $Ag(NO_3)_2$) and dried overnight at 383 K. The metal loading (determined with AAS analysis on the basis of dehydrated zeolite) was as follows: CoNaY 3.8 wt% (1 Co/supercage), CoCaY 5.4 wt% (1.5 Co/supercage), NiNaY 3.7 wt% (1 Ni/supercage). All catalysts were pressed, ground, and sieved to obtain a particle size fraction of 125–425 $\mu$m. The samples were stored in a desiccator over a saturated $CaCl_2$ solution.

NaY was also loaded with Co by gas phase adsorption (GPA). Dehydrated NaY ($125 < d_p < 425$ $\mu$m) was contacted with the vapor of $Co(CO)_3NO$ in vacuum (313 K). Subsequently, the prepared sample was heated overnight at 333 K in a vacuum-sealed ampoule. The sample contained (determined by AAS analysis) 4.5 wt% Co (1.5 Co/supercage).

The sulfidation procedure depended on the preparation method. The samples prepared by ion exchange were dehydrated by heating to 673 K in He (6 K/min, 60 ml/min), cooled or heated (when necessary) to the desired sulfidation temperature (between 473 K and 773 K) and sulfided *in situ* for 2 h in 10% $H_2S/H_2$ (60 ml/min). In some cases the sulfidation time was varied. The samples prepared by gas phase adsorption were transported via a nitrogen recirculation glove box ($O_2$ and $H_2O < 2$ ppm) to the equipment without exposure to air. The samples were treated for 15 min in 10% $H_2S/H_2$ (60 ml/min) at 298 K and heated with 2 K/min to 473 K in the same gas mixture. Subsequently, the samples were heated (when necessary) to the desired sulfidation temperature with 6 K/min and treated for 2 h at this temperature. Sulfidation temperatures between 473 and 773 K were applied.

The catalysts will be denoted as CAT(a, b, c, d) with CAT standing for CoNaY, CoCaY, or NiNaY to indicate preparation by ion exchange and Co(GPA)NaY to indicate preparation by gas phase adsorption. The characters a, b, c, and d stand for treatment before sulfidation, sulfidation temperature, sulfidation time, and treatment after sulfidation, respectively. When the standard sulfidation procedure (dehydration before sulfidation, 2 h sulfidation, and no additional treatment after sulfidation) is used only the sulfidation temperature will be given, e.g., CoNaY (673 K). For comparison, some samples were sulfided in the presence of physisorbed water by heating from 298 K to the desired sulfidation temperature with 6 K/min in 10% $H_2S/H_2$ and 2 hours at this temperature. The presence of physisorbed water before and during sulfidation (a) will be indicated by addition of wet before the sulfidation temperature, e.g., CoNaY (wet, 673 K).

The sulfidation time (c), when different from 2 h, will be indicated behind the sulfidation temperature, e.g., CoNaY (673 K, 20 h). In some cases, additional treatments were performed between the sulfidation step and the HDS measurements. These additional treatments (d) will be indicated behind the sulfidation temperature, $NH_3$ for ammonia treatment (e.g., CoNaY (573 K, $NH_3$)), and $H_2O$ for water treatment (see the thiophene HDS experimental section for a description of the treatment).

### *Catalytic Activity*

Thiophene HDS activity measurements were carried out in a microflow reactor under standard conditions (1 bar, 673 K, 50 ml/min, 4% thiophene/$H_2$). The catalysts containing 25 wt% water (CoNaY (100 mg) or CoCaY (50 mg)) were mixed with SiC to obtain a catalyst bed of 1.5 cm and placed in the HDS equipment.

Co(GPA)NaY (100 mg) was transferred via a glove box in an *in situ* reactor and placed in the HDS equipment without exposure to air. The samples were sulfided as described in the sulfidation section. Some freshly sulfided CoNaY and NiNaY samples (200 mg) were additionally treated with $NH_3$ or $H_2O$. The $NH_3$ treatment was carried out as follows. After 2 h sulfidation at 573 K, the sample was cooled to 523 K in 10% $H_2S/H_2$ (6 K/min, 60 ml/min), treated for 1 h with a flow of $NH_3$, cooled in He (60 ml/min) to 298 K, and flushed for 2 h. The $H_2O$ treatment was carried out as follows. After 2 h sulfidation at 573 K, the sample was cooled to 298 K in 10% $H_2S/H_2$ (6 K/min, 60 ml/min) and flushed with humidified He (60 ml/min, 1 h). He was humidified by bubbling through water at 298 K. After each treatment ($NH_3$ or $H_2O$) the catalysts were again sulfided in 10% $H_2S/H_2$ at 573 K (6 K/min, 60 ml/min, 2 h).

When the sulfidation step was completed, the samples were heated or cooled (when necessary) from sulfidation temperature to 673 K in 10% $H_2S/H_2$ at a rate of 6 K/min. At 673 K the flow was switched to the thiophene/$H_2$ flow. Reaction products were analyzed by on-line GC analysis. The first sample was taken after 2 min reaction time and the following ones at intervals of 35 min. Besides $C_4$ products, a considerable amount of coke and cracking products was formed due to the presence of Brønsted acid sites. Therefore, thiophene converted to any of the reaction products including coke was taken into account for the calculation of the HDS reaction rate constant ($k_{\mathrm{hds}}$) assuming the reaction to be of first order in thiophene (17). Coke formation, which often causes strong deactivation due to shielding of the metal sulfide phase, can severely hamper the evaluation of the intrinsic properties (2, 7). Therefore we compared in the discussion the catalysts on the basis of their activity at a very short run time (initial activity after 2 min run time). Due to the sometimes very strong deactivation at short run times, the reproducibility of the initial activity was less than for steady state activities but still sufficient to compare the intrinsic activities of the catalysts with each other (the initial HDS activity was reproducible within 10%). In addition, the activity of Co/C (3.2 wt% Co prepared according to the procedure as described by Vissers *et al.* (18)) and of the CaY support were measured.

### *Chemical Sulfur Analysis*

The S/Co ratio of CoCaY sulfided at different temperatures was determined by chemical sulfur analysis. In order to remove physisorbed $H_2S$, the freshly sulfided samples were flushed in He at 298 K for 2 h prior to sulfur analysis. Already after 30 min all physisorbed $H_2S$ was removed (13). Subsequently, all Co species (unsulfided and sulfided) present were dissolved in nitric acid while the mixture was carefully heated. During this process the sulfided species were converted to Co sulfate. The Co content was determined by AAS and the amount of sulfate was determined by titration with barium perchlorate.

### *Temperature Programmed Techniques (TPS and Ar-TPT)*

Two different temperature programmed treatments were used. The sulfidation of CoCaY was monitored by temperature programmed sulfidation. The protolysis reaction of sulfided CoCaY was studied by temperature programmed treatment with Ar (Ar-TPT) (13). The facility has been described elsewhere (19, 20). The TPS experiments were carried out according to the following procedure. A catalyst sample (350 mg) was heated in Ar (60 ml/min, 6 K/min, from 298 to 673 K, 0.5 h at 673 K) for dehydration. After cooling to 298 K Ar was replaced by $H_2S/H_2/Ar$ (3.3%, 28.1%, 68.6%) and the sample was sulfided (60 ml/min, 6 K/min from 298 to 1273 K, 2 h at 1273 K). The $H_2S$ concentration at the reactor outlet was measured by a UV spectrophotometer at 195 nm during the complete treatment. The Ar-TPT measurements were carried out after sulfidation at 673 K according to the same procedure with the only difference being that the sample was heated to 673 K and treated 2 h at 673 K in the sulfidation mixture. After cooling to 298 K the sample was flushed with Ar (60 ml/min) till no $H_2S$ was measured at the reactor outlet. Subsequently, the sample was heated to 1273 K (6 K/min) in Ar while the $H_2S$ concentration in the reactor outlet was measured by a UV spectrophotometer at 195 nm.

### *Transmission Electron Microscopy (TEM)*

The distribution of the metal sulfide over the zeolite of Co(GPA)NaY (473 K), Co(GPA)NaY (773 K), CoNaY (573 K, $NH_3$), and NiNaY (573 K, $NH_3$) was studied by TEM. The Co(GPA)NaY catalysts were freshly sulfided for the TEM measurements while the ammonia treated catalysts were measured after 2.5 h HDS reaction. The sulfided catalysts were, without exposure to air, transferred to a glove box after the pretreatment (sulfidation or HDS). In this glove box the samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground samples in *n*-hexane on the grid, followed by drying in ambient conditions. Samples were transferred to the transmission electron microscope (Philips CM 30 T with a $LaB_6$ filament as the source of the electrons operated at 300 kV) in a special vacuum-transfer sample holder under exclusion of air. Energy dispersive X-ray elemental analysis (EDX spectroscopy) was performed using a LINK EDX system.

## RESULTS

### *Catalytic Activity*

The initial thiophene HDS activities of CoNaY, CoCaY, and Co(GPA)NaY as a function of sulfidation temperature are compared in Fig. 1. The activity of CoCaY was clearly higher than that of CoNaY and both showed a similar dependency on the sulfidation temperature. High initial activities were observed up to a sulfidation temperature of 573 K, whereas at higher sulfidation temperatures the activity strongly decreased. Increasing the sulfidation time at 673 K from 2 to 20 h resulted in a further activity decrease. The activity decrease with increasing sulfidation temperature as well as with increasing sulfidation time for CoNaY was relatively larger than that of CoCaY. In addition, CoCaY (673 K, 20 h) had a black color in contrast to the blue color of CoNaY (673 K, 20 h).

It is evident from Fig. 1 that the initial activity of Co(GPA)NaY was much lower than that of CoNaY and CoCaY at all sulfidation temperatures. Up to a sulfidation temperature of 573 K the activity was constant followed by a decreasing activity after higher sulfidation temperatures.

The catalytic activity as a function of run time of Co(GPA)NaY was clearly different from that of CoNaY and CoCaY and showed a rather stable activity like Co/C (Fig. 2). In addition, the product distribution of the catalysts prepared by gas phase adsorption and ion exchange was clearly different. Co(GPA)NaY formed mainly $C_4$ products (95%), while over CoNaY and CoCaY initially mainly cracking, polymerization, and coking products and only 25–30% $C_4$ products were formed. Furthermore, it can be observed that CoCaY deactivated much faster than CoNaY. For Ni zeolite catalysts (NaY, CaY, and HY) it was concluded that the deactivation during run time should be ascribed to coke formation and is strongly related to the acidity (2, 7).

The effect of different treatments before and after the sulfidation on the activity of CoNaY and NiNaY are compared in Figs. 3a and 3b, respectively. The highest activity was found for CoNaY and NiNaY, which were dehydrated before sulfidation. Treatment with water after sulfidation had a large negative influence on the thiophene HDS activity. The initial HDS activity of CoNaY (573 K, $H_2O$) and NiNaY (573 K, $H_2O$) was lower than the activity of CoNaY (573 K) and NiNaY (573 K). Ammonia treatment after sulfidation had an enormous negative influence on the HDS activity. The initial HDS activity of CoNaY (573 K,

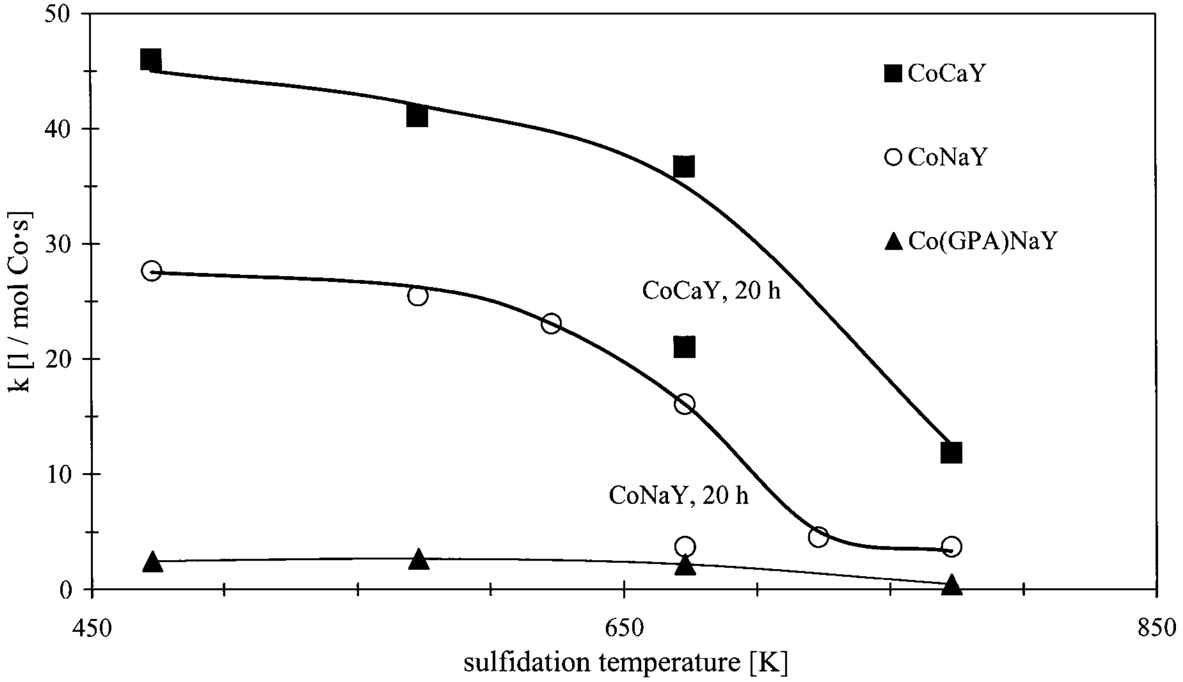

**FIG. 1.** Initial thiophene HDS activity of CoCaY, CoNaY, and Co(GPA)NaY as a function of the sulfidation temperature.

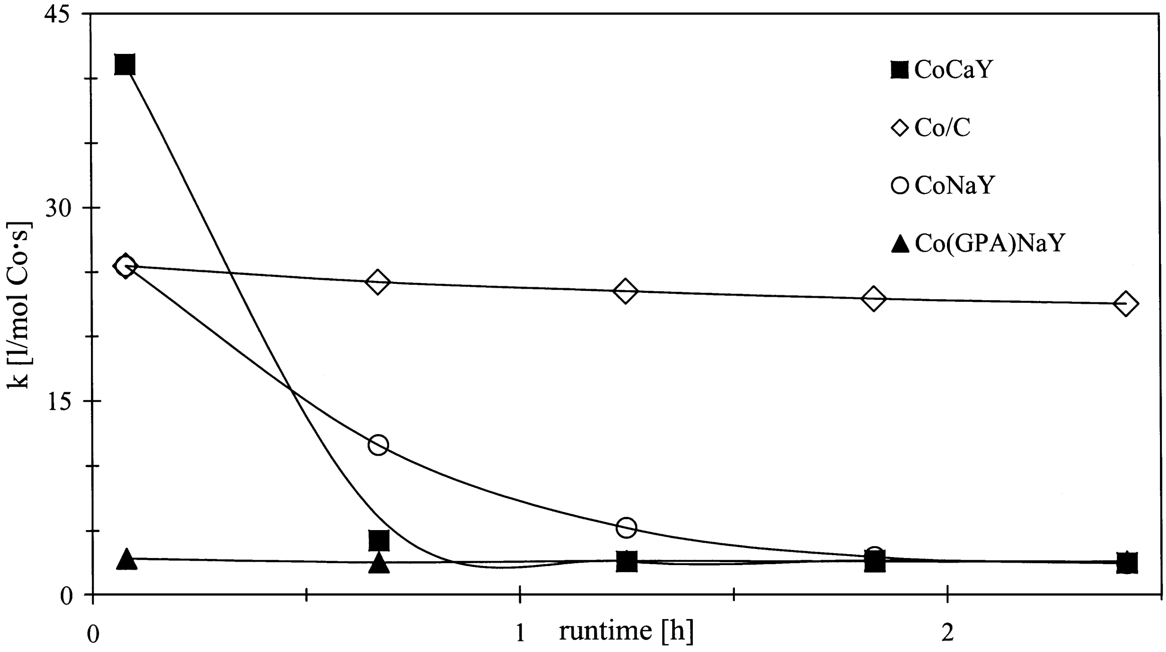

**FIG. 2.** Thiophene HDS activity of CoCaY (573 K), Co/C (673 K), CoNaY (573 K), and Co(GPA)NaY (573 K) as a function of run time.

$NH_3$) and NiNaY (573 K, $NH_3$) was very low. The catalytic behavior of CoNaY (573 K, $NH_3$) and NiNaY (573 K, $NH_3$) showed a large similarity with CoNaY (wet, 573 K) and NiNaY (wet, 573 K), respectively.

### *Chemical Sulfur Analysis*

The S/Co ratio and color of CoCaY and for comparison those previously (3) determined for CoNaY sulfided at different temperatures are collected in Table 1.

CoNaY and CoCaY showed clearly a different sulfidation behavior. The S/Co ratio of CoNaY continuously decreased with increasing sulfidation temperature, while the S/Co ratio of CoCaY decreased only after sulfidation above 673 K. The different behavior is also reflected in the color of the catalysts. CoNaY had a blue color after sulfidation at 773 K, while CoCaY remained black after sulfidation at this temperature. It should be noted that both support materials (NaY and CaY) remained white after sulfidation at 673 K and no S could be determined by the chemical analysis.

### *Temperature Programmed Techniques (TPS and Ar-TPT)*

With the exception of a very large negative peak at 298 K caused by $H_2S$ adsorption (physisorption and chemisorption), the TPS pattern of CoCaY is depicted in Fig. 4. This pattern is roughly the same as measured for CoNaY (3). The first peak is a large positive peak with a maximum at 330 K. A small negative peak can be observed with a minimum at 510 K. The first (positive) and second (negative)

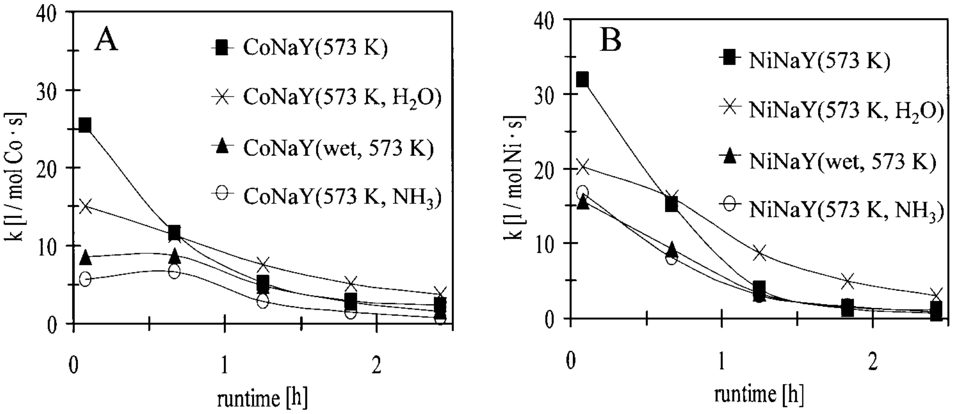

**FIG. 3.** Thiophene HDS activity after different treatments before and after sulfidation (A) CoNaY and (B) NiNaY.

**TABLE 1**

**S/Co Ratio and Color of Co(5.4)CaY and Co(4)NaY after Sulfidation at Different Temperatures**

| Sulfidation temperature | CoCaY | CoNaY |
|---|---|---|
| Fresh | 0<br>(Purple) | 0<br>(Purple) |
| 473 K | 1.01<br>(Black) | 0.90<br>(Black) |
| 673 K | 1.04<br>(Black) | 0.75<br>(Black) |
| 773 K | 0.77<br>(Black) | 0.65<br>(Blue) |

peak reflect the overall result of desorption of excess $H_2S$ and $H_2S$ uptake required for Co sulfide formation. It was difficult to interpret the rest of the pattern, because the base line slightly increased and fluctuated. It can be suggested that the pattern contained two broad peaks with a maximum at 860 K and a minimum at 910 K. The TPS pattern of CaY (not shown) showed only $H_2S$ physisorption and chemisorption at room temperature and $H_2S$ desorption with a maximum at 330 K.

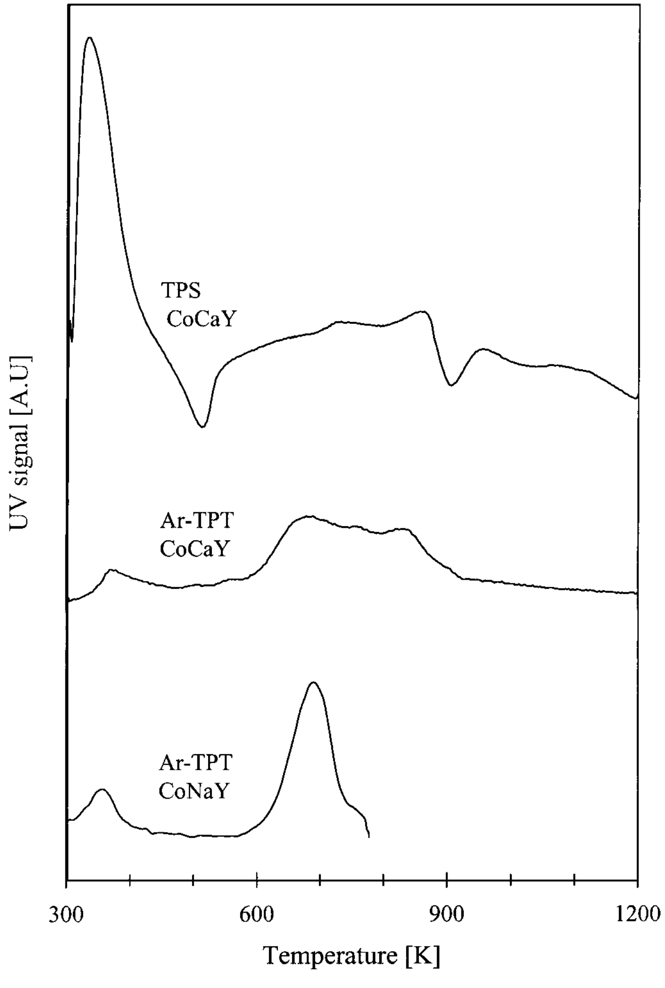

**FIG. 4.** TPS of CoCaY and Ar-TPT of CoCaY (673 K) and CoNaY (673 K). A negative peak means $H_2S$ consumption/adsorption and positive peak means $H_2S$ production/desorption.

In addition, $H_2S$ production during heating of sulfided CoCaY in Ar (Ar-TPT) was monitored (Fig. 4). The Ar-TPT pattern showed two $H_2S$ desorption peaks: one small peak with a maximum at 370 K and another broad $H_2S$ production peak with one or more maxima between 680 and 830 K. For comparison the Ar-TPT pattern of sulfided CoNaY (13) is also shown in Fig. 4.

### *Transmission Electron Microscopy (TEM)*

For Co(GPA)NaY (473 K) and Co(GPA)NaY (773 K) Co sulfide particles were observed at the external zeolite surface. EDX analysis showed the presence of Co and S in areas where these Co sulfide particles were observed as well as in areas where only the zeolite lattice was observed. More and larger particles at the external zeolite surface were observed for Co(GPA)NaY (773 K) than for Co(GPA)NaY (473 K). A TEM image of Co(GPA)NaY (773 K) is shown in Fig. 5.

For NiNaY (573 K, $NH_3$) as well as CoNaY (573 K, $NH_3$) many particles of different size with a higher contrast than the zeolite were observed throughout the sample. These particles were located at the external surface of the zeolite crystals and EDX analysis of these crystals showed a much higher concentration of S and Co(Ni) than in the bulk of the material. In the case of CoNaY (573 K, $NH_3$), some clusters of $CoS_x$ particles were observed that do not seem very much in contact with the zeolite anymore. The EDX analysis of such an almost separated phase showed that it consists mainly of Co and S. An example of a TEM image of NiNaY (573 K, $NH_3$) together with the EDX spectra of the zeolite bulk (A) and a Ni sulfide particle at the external zeolite surface (B) is presented in Fig. 6.

## DISCUSSION

### *Prevention of Protolysis*

The initial thiophene HDS activity of CoNaY strongly decreases with increasing sulfidation temperature (Fig. 1). This was ascribed to a protolysis reaction and hampers the preparation of well defined metal sulfide particles under reaction conditions (3). A possible way of avoiding the protolysis reaction can be to prevent the formation of the stable blue product. It was suggested (3) that the protolysis product in CoNaY migrated to the sodalite cages. Maybe blocking the cation sites in the sodalite cages and the hexagonal prisms by, e.g., $Ca^{2+}$ ions could prevent the formation of the protolysis product. For this reason, the properties of CoCaY during and after sulfidation were studied. The

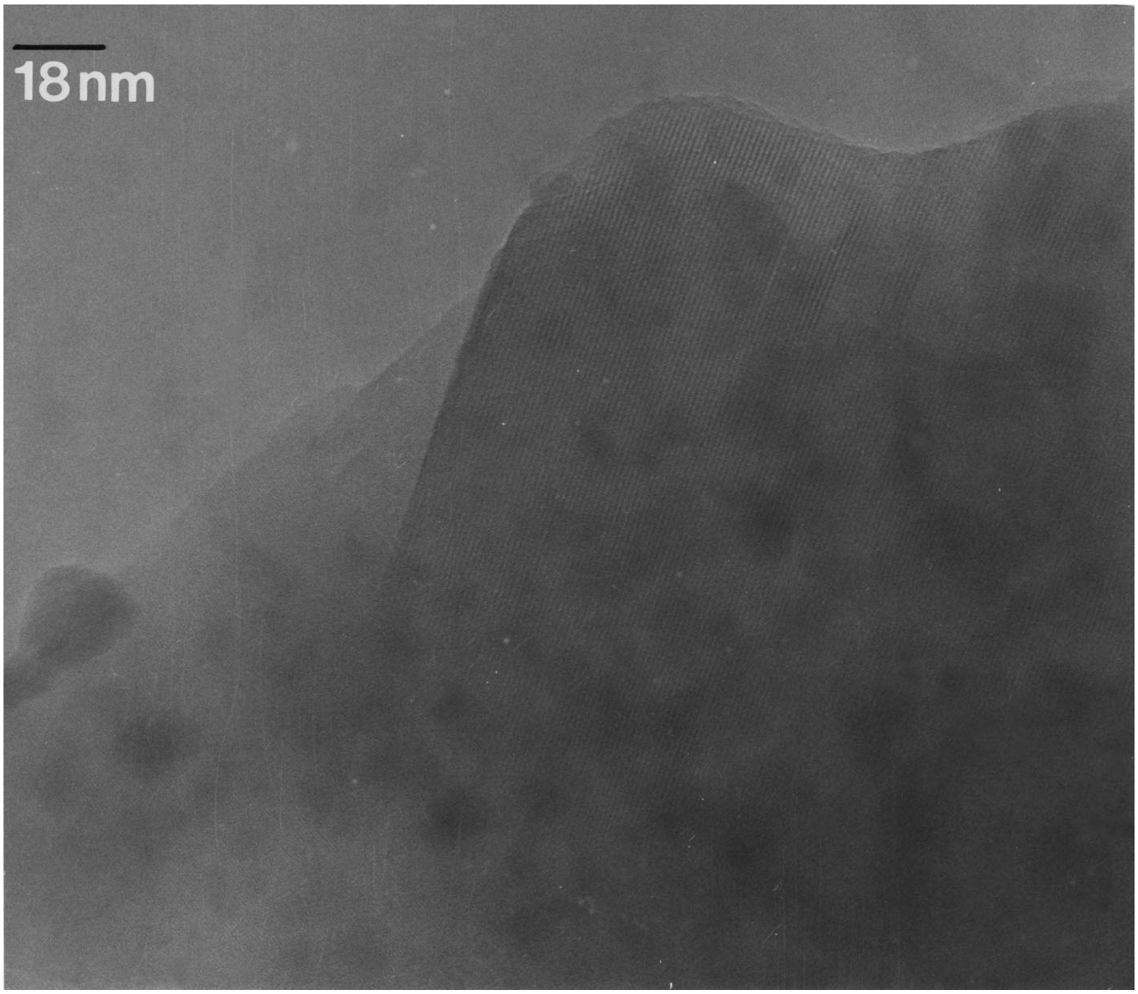

**FIG. 5.** TEM image of Co(GPA)NaY (773 K).

Ar-TPT pattern of CoNaY and CoCaY were clearly different (Fig. 4). A $H_2S$ production peak starting around 573 K was observed in both patterns. However, the maximum of this peak for CoNaY was around 680 K but for CoCaY the peak was much broader and showed no clear maximum. This means that during a larger temperature range $H_2S$ was produced. In other words, more time was required to complete the protolysis reaction. The chemical sulfur analysis strengthened this suggestion (see Table 1). It was observed that the S/Co ratio started to decrease at sulfidation temperatures above 573 K for CoNaY, while for CoCaY the S/Co ratio was constant till a sulfidation temperature of 673 K. Besides, CoNaY (673 K, 20 h) changed from black to blue color during sulfidation, in contrast to CoCaY (673 K, 20 h), which remained black.

The thiophene HDS activity data were in agreement with this conclusion. The HDS activity of CoNaY decreased faster and to a larger extent than those of CoCaY as is unquestionably illustrated when relative initial HDS activities (with the activity after sulfidation at 573 K as 100%) are compared (Fig. 7).

This different behavior of CoNaY and CoCaY can be explained by the following model in which sulfidation–protolysis is considered to be an equilibrium reaction. It is clear from the Ar-TPT patterns that the protolysis reaction started at temperatures higher than 573 K. In the case of CoNaY (673 K) the protolysis was not completed. The catalyst was black and showed thiophene HDS activity. CoNaY (673 K, 20 h) had the same low HDS activity and blue color as CoNaY (773 K). Clearly, sulfidation time and temperature are important parameters to complete the protolysis reaction. This suggests that besides the decomposition a slow reaction (e.g., solid state reaction) takes place. It can be imagined that the formed Co product has two possibilities: to resulfide with $H_2S$ or to migrate from the supercages to the sodalite cages. When the protolysis has been completed all the Co sulfide particles have fallen apart and the product occupies cation sites in the sodalite cages. The catalyst will be blue and shows no thiophene HDS activity.

In the case of CaY a part of the sodalite cages and hexagonal prisms was occupied by $Ca^{2+}$ cations (14). Most

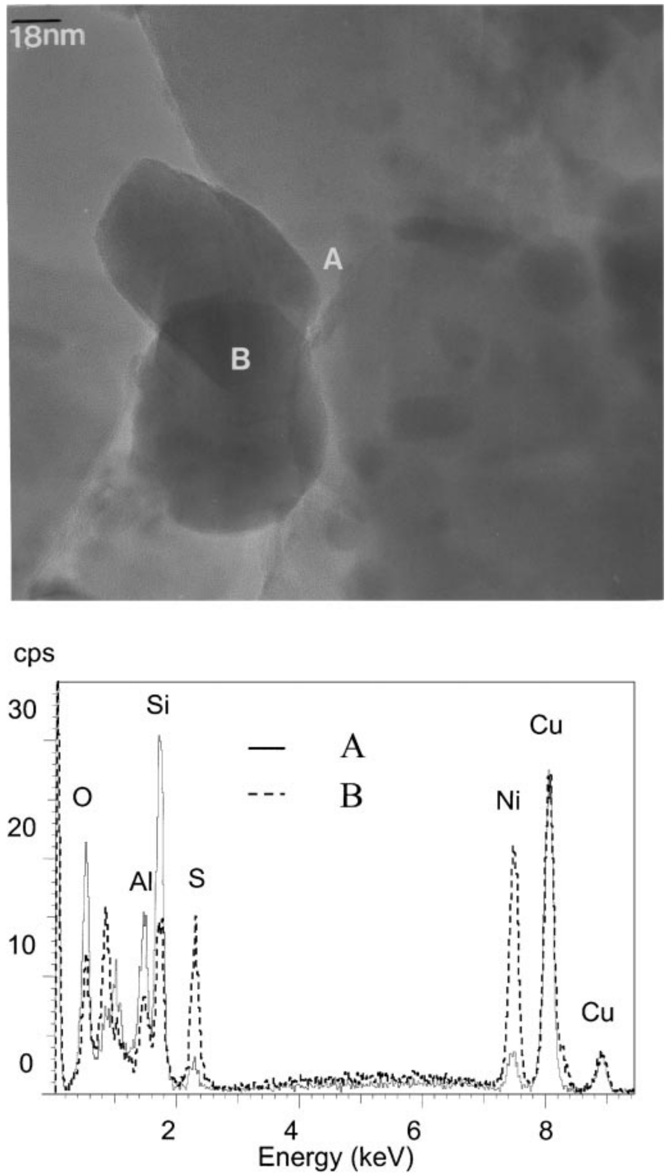

**FIG. 6.** TEM image and EDX spectra of NiNaY (573 K, NH$_3$). The areas measured for EDX spectra are indicated in the image, viz. (A) zeolite bulk and (B) Ni sulfide particle at the external zeolite surface. Cu is originating from the TEM grid.

likely, no protolysis products can migrate to the sodalite cages occupied by Ca$^{2+}$. The protolysis reaction in CoCaY starts also at 573 K. The formed Co product has the same two possibilities (resulfidation or migration). A larger part of the Co product will resulfide than in the case of CoNaY because of a part of the sodalite cages is blocked by Ca. Possibly, the Co sulfide particles shift (meanwhile decomposition and resulfidation occur) through the supercages till an empty sodalite cage comes across. In this case, sulfidation time and temperature are even more important than in CoNaY to complete the protolysis reaction.

In conclusion, the negative effect of the protolysis reaction as observed for CoNaY (3) can be retarded by blocking the sodalite cages by Ca$^{2+}$ cations. The reaction cannot completely be prevented since in CoCaY prepared by ion exchange Ca$^{2+}$ occupies not all sodalite cages. The retardation in CoCaY results from the availability of less empty sodalite cages in CaY to stabilize the formed protolysis product.

Another way of preventing the protolysis reaction is avoiding proton formation during sulfidation for instance via the use of carbonyl complexes, e.g., Co(CO)$_3$NO (15, 16). Although the color of Co(GPA)NaY after sulfidation gives no indication for the occurrence of protolysis (the catalysts were black after all sulfidation temperatures) the HDS activity is decreasing with increasing sulfidation temperature. The product selectivity (nearly exclusive C$_4$ formation) indicates that a nonacidic catalyst had been prepared. So, protolysis as explanation for the decreasing activity is unlikely. As can be concluded from the TEM measurements, the Co(CO)NO$_3$, gas phase adsorption preparation method results after sulfidation in the presence of Co sulfide particles at the external zeolite surface as well as inside the cavities. Most probably, the metal sulfide can move through the pores and finally sinters at the external surface. The mobility increases with increasing sulfidation temperature, explaining the observation that after sulfidation at 773 K more and larger particles having a lower HDS activity were observed. Our findings with the Co(CO)$_3$NO type catalysts do not seem to be in line with those of Okamoto and Katsuyama (15, 16). From EXAFS data they concluded that the Co sulfide species prepared using Co(CO)$_3$NO are highly dispersed inside the NaY structure in contrast to Co sulfide species prepared using Co$_2$(CO)$_8$, which are believed to be located at the external NaY surface and thus liable to sintering. However, the thiophene HDS activities they show for both types of catalysts are very much comparable. They ascribed the high HDS activity of the catalyst prepared by Co(CO)$_3$NO to a high dispersion but they have no explanation for the slightly higher activity of the catalyst prepared using Co$_2$(CO)$_8$ in which Co sulfide is present as large particles at the external zeolite surface. Their activity data suggest that the Co sulfide species present in their Co(CO)$_3$NO derived catalyst are also (partially) located at the external zeolite surface.

### *The Effect of Protons on the Activity*

Clearly thiophene HDS activity differences were observed for CoNaY, CoCaY, and Co(GPA)NaY catalysts. These catalysts differ in amount of protons. Zhang *et al.* (10) suggested that protons act as an anchor for Pd particles in zeolite. The protolysis reaction and the observation that the sulfide particles remained in the zeolite when the sulfidation was carefully applied suggest that also an interaction between metal sulfides and zeolite protons exist. This is in line with results found by Breysse *et al.* (8) that an interaction

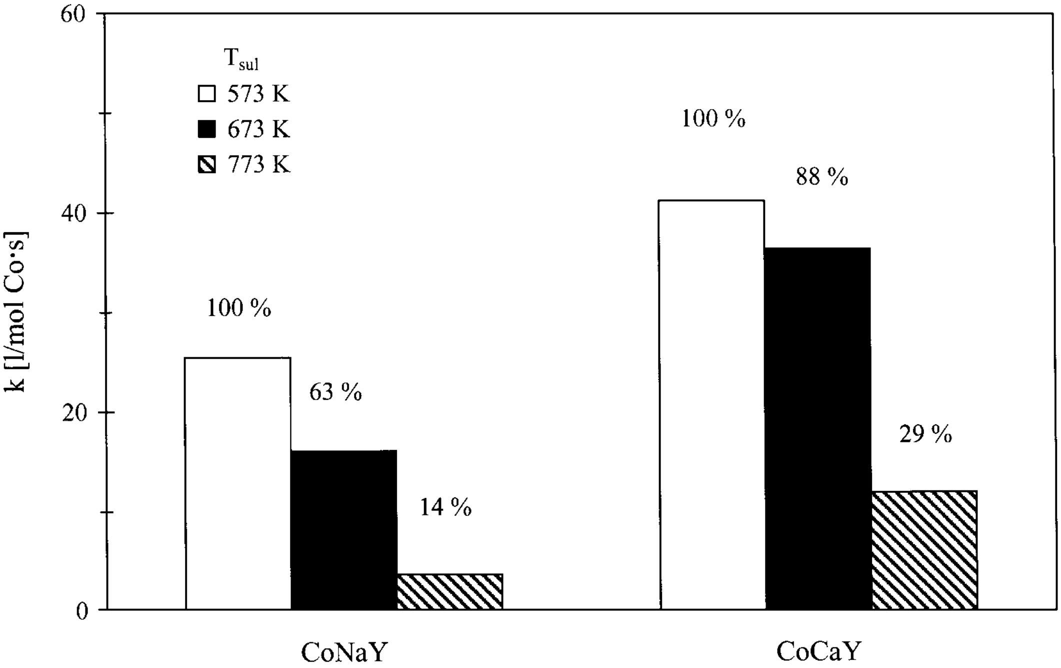

**FIG. 7.** Relative and absolute initial thiophene HDS activities of CoNaY and CoCaY as a function of sulfidation temperature.

between protons and Ru sulfide changes the catalytic properties of the Ru sulfide. To check the proposition of a $H^+$–TMS interaction, CoNaY and NiNaY prepared by ion exchange were sulfided, during this reaction protons and metal sulfides were formed in the supercages. Subsequently, the catalysts were treated with a base. According to Zhang *et al.* (10) the base reacts with the proton, the interaction between the proton and Pd is broken, and Pd sinters on the external zeolite surface. In our case, a dramatic decrease of the initial thiophene HDS activity was measured for CoNaY (573 K) and NiNaY (573 K) after treatment with a base ($H_2O$ or $NH_3$) (Figs. 3a and 3b). The strongest effect was observed after treatment with $NH_3$. The activity of NiNaY (573 K, $NH_3$) was similar to that of NiNaY (wet, 573 K) and that of CoNaY (573 K, $NH_3$) was only slightly higher than that of CoNaY (wet, 573 K). It is known that wet sulfidation (sulfidation in the presence of physisorbed water) resulted in the formation of large metal sulfide particles on the external zeolite surface with a low thiophene HDS activity (7, 11). In case of CoNaY (573 K) (so sulfided after dehydration) no Co sulfide particles were observed at the external zeolite surface. NiNaY (573 K, $NH_3$) and CoNaY (573 K, $NH_3$) were examined with TEM after the HDS reaction. In both samples many metal sulfide particles were observed at the external surface. So it can be concluded that an interaction between metal sulfides and zeolite protons exists which is broken by treatment with a base resulting in the migration of the metal sulfide to the external surface. The observation that the effect of treatment with $H_2O$ on the activity is much less than those of treatment with $NH_3$ may be explained by the fact that $H_2O$ is a weaker base than $NH_3$. Another explanation can be that the treatment temperature with $NH_3$ was higher (523 K) than that (298 K) with $H_2O$.

The observation that the protons act as an anchor for the metal sulfide has important consequences for the preparation and possible applications of zeolite-supported metal sulfides.

Summarizing our contributions (3, 7, 11–13, 21–24) concerning the preparation of zeolite-supported metal sulfides prepared by sulfidation of Co or Ni ion exchanged zeolite Y (denoted as CoNa(Ca)Y or NiNa(Ca)Y) and by sulfidation of Co or Ni impregnated on zeolite Y (denoted as Co/Na(Ca)Y(imp) or Ni/Na(Ca)Y(imp)), it can be concluded that an interaction between the metal precursor and the zeolite lattice is important to prepare well-defined particles inside the zeolite cages. It is important to note that impregnation is indicated by / between metal and zeolite and addition of imp behind the catalyst notation. In the case of a non-acidic zeolite (Co(GPA)NaY), the Co sulfide migrates to the external surface during sulfidation due to absence of an interaction with the zeolite. Also, sulfidation in the presence of physisorbed water results in the formation of the metal sulfide on the external zeolite surface independent of the preparation method (impregnation or ion exchange) (7, 11, 21, 22). The hydrated cations/metal oxides are disconnected from the zeolite lattice and during sulfidation the sulfide migrates out of the zeolite cavities to form large stable clusters at the external surface.

An interaction between the metal precursor and the zeolite can be obtained by dehydration. The interaction is not strong enough to keep the metal sulfide during sulfidation in the zeolite when impregnation is used as a method of introducing the metal into the zeolite. It was found that after sulfidation at 473 K of Co impregnated on NaY (Co/NaY(imp)) small Co sulfide particles were formed, mainly inside the zeolite (22). However, after sulfidation at 673 K 76% $Co_9S_8$ was formed and only 24% was present as small Co sulfide particles (22). A lot of Co sulfide particles were observed on the external surface by TEM measurements (22). Also for Ni impregnated on NaY (Ni/NaY(imp)), large Ni sulfide particles were found on the external surface after sulfidation at 673 K (7). Probably, a higher sulfidation temperature accelerates the migration to the external surface, possibly enhanced by the formation of water during sulfidation of the metal oxides.

Dehydration of zeolite supported metal ions prepared by ion exchange results in an interaction between the metal ion and the zeolite. The differences in metal sulfide distribution and activity found for dehydrated sulfided and $NH_3$ treated dehydrated sulfided catalysts strongly suggest that after sulfidation an interaction still exists. This interaction retains the metal sulfide in the zeolite pores. Interestingly, a larger part of small Co sulfide particles was found (40% vs 24%) after sulfidation at 673 K of Co impregnated on CaY (Co/CaY(imp)) instead of on NaY (Co/NaY(imp)) (22). Several possible explanations were given in this publication (22) for the more dispersed Co sulfide system in impregnation type Co/CaY(imp) than in impregnation type Co/NaY(imp). The importance of the $H^+$–TMS interaction in the ion-exchanged system indicates that the explanation based on a possible interaction in Co/CaY(imp) should be considered seriously. The observed $Co_9S_8$ particles at the external surface of Co/CaY(imp) (22) can be explained by the formation of water during sulfidation that reduces the interaction.

The strength of the interaction depends on the sulfidation temperature, metal, and support. The proton–metal sulfide interaction changes significantly at higher sulfidation temperatures. For Co/CaY(imp) (sulfidation temperature higher than 473 K) and NiNaY (sulfidation temperature higher than 573 K) the interaction between protons and metal sulfides is weakened at higher temperatures, resulting in migration. For CoNaY (sulfidation temperature higher than 473 K) and CoCaY (sulfidation temperature higher than 673 K) the interaction increases and protons irreversibly react, resulting in decomposition of the Co sulfide particles and migration into the sodalite cages.

The role of protons as an anchor to keep the metal sulfide in the zeolite pores has also an important limitation for industrial use. The interaction is broken by bases (like nitrogen compounds and water) resulting in sintering of the metal sulfide at the zeolite external surface. Crude oil always contains traces of nitrogen compounds and water. For this reason CoNaY and NiNaY are not attractive for use in a refinery. However, zeolites are still very interesting for studying practical questions with well-defined catalysts.

Such a question is the role of the protons in hydrodesulfurization. To answer this question Co loaded zeolites with different acidity were sulfided viz. Co(GPA)NaY(no acidity), CoNaY, and CoCaY and tested in thiophene HDS. The nearly exclusive formation of $C_4$ products and the absence of cracking, polymerization, and isomerization products for Co(GPA)NaY indicate that a nonacidic catalyst has been formed. It is known (7) that CaY shows a much higher acidity than NaY due to the formation of acid sites by protolysis of water molecules adsorbed on the $Ca^{2+}$ ions. Indeed, it was found (7) by ethylamine desorption that Ni/CaY(imp) was much more acidic than Ni/NaY(imp). The observed deactivation behavior as a function of run time for CoNaY and CoCaY is also in line with a higher acidity for CoCaY (see Results). The activities as a function of run time are presented in Fig. 2. The initial activity of Co(GPA)NaY(573 K), CaY(573 K), and CoCaY(573 K) are presented in Fig. 8. It should be noted that in Fig. 8 the $k_{\mathrm{hds}}$ is expressed in $10^{-3}$ $m^3/(\mathrm{kg\ cat} \cdot s)$ instead of $L/(\mathrm{mol\ Co} \cdot s)$.

The activity difference of CoNaY (573 K) and CoCaY (573 K) (Fig. 2) cannot be explained by an improvement of the dispersion. It was concluded from an EXAFS study (23) on the sulfidation of CoNaY that no Co–Co contribution was present after dry sulfidation. That indicates that very small Co sulfide clusters are formed. Smaller particles consisting of less than one Co are impossible, so the activity increase going from CoNaY to CoCaY should be caused by something else. In addition, the lumped activity of Co(GPA)NaY (573 K) and CaY (573 K) (two separate reactors) is obviously lower than that of CoCaY (573 K). The Co sulfide phase and protons clearly show a synergetic effect. Although, Co(GPA)NaY (Co sulfide particles were observed at the external surface) and CoCaY (Co sulfide is anchored by the protons in the zeolite cavities) had a different dispersion, it looks unlikely that the very large activity difference is only caused by dispersion difference. Welters *et al.* (2) showed that the thiophene HDS activity increases with increasing numbers of protons and gave several possible explanations. The explanations based on thiophene adsorption reservoir or acceleration of the rate-determining step seems unlikely considering the negative effect of protons on the HDS activity of MoHY although most probably a large part of the $MoS_2$ is located in the neighborhood of the protons (24). On the other hand, the explanation of changing the catalytic properties seems likely. Possibly, the protons affect the electronic structure of Co sulfide like in Ru sulfide (8) where the electron-deficient character of Ru sulfide increases due to the Ru sulfide proton interaction. Following the same line of reasoning the Co sulfide would become more electron deficient due to the interaction with protons. Different explanations about the reason why electron-deficient character has a positive

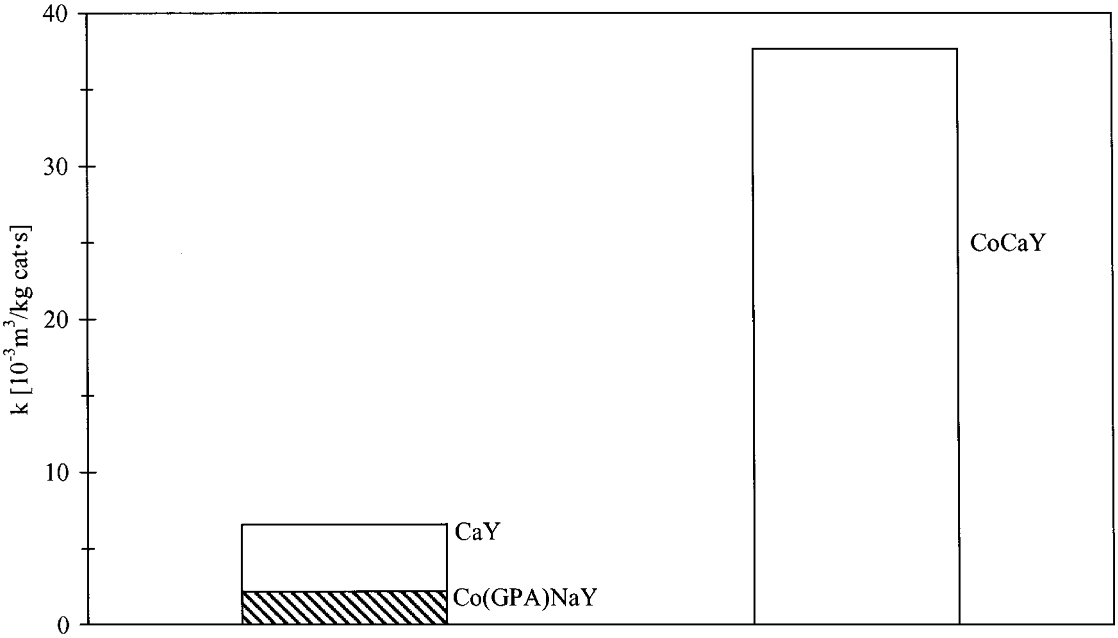

**FIG. 8.** Initial thiophene HDS activity of CoCaY (573 K) compared with the lumped activity of Co(GPA)NaY (573 K) and CaY (573 K). Note that the $k_{\mathrm{hds}}$ is expressed in $10^{-3}$ $m^3/(kg\ cat \cdot s)$.

effect on the activity can be found in literature. Nørskov *et al.* (25) stated that the activity is related to the ability of the TMS to form sulfur vacancies. The TMS with the lowest metal sulfur bond energy will have the highest activity. An interaction between protons and the metal sulfide will cause a weakening of the Co–S bond, resulting in an increase in activity. The higher activity of CoCaY could then be explained by a stronger interaction due to a higher acidity. In contrast, Wiegand and Friend (26) suggested that a strong interaction between thiophene and the TMS results in a high activity due to activation of the S–C bond. Smit and Johnson (27) showed in a theoretical study that the interaction between sulfur of thiophene and the TMS is a good parameter for the HDS activity. Hensen *et al.* (28) concluded from a kinetic study that a high thiophene HDS activity is linked to a strong TMS–thiophene interaction. The interaction between a proton and Co sulfide will increase the electron-deficient character of the TMS, resulting in a stronger interaction with thiophene and following the above line of reasoning in a higher activity.

A second practical question is the dependence of specific activity on particle size. In Fig. 2 the activities of Co(GPA) NaY (573 K), CoNaY (573 K), and CoCaY (573 K) are compared with that of Co/C (673 K). The initial activity of CoNaY is comparable with Co/C, while according to EXAFS measurements the dispersion of the zeolite-supported Co sulfide (no Co–Co neighbors (23)) is much higher than the dispersion of the carbon-supported Co sulfide ($N_{\mathrm{Co–Co}} = 2.7$) (29). In addition, Crajé *et al.* (29) showed by MES measurements that the QS increased with decreasing Co loading, indicating that smaller and/or less ordered Co sulfide particles were formed at lower loading. Hensen (30) showed that the thiophene HDS activity of Co/C increased with decreasing Co loading (and thus increasing dispersion). So, when Co/C catalyst with a Co loading lower than 3.2 wt% are compared with CoNaY, CoNaY has a lower activity (per Co) than Co/C in spite of the extremely high Co sulfide dispersion in the zeolite. Possibly, Co sulfide clusters of a certain size have to be present for a high thiophene HDS activity (in other words, there is an optimum in dispersion). However, it cannot be excluded that the C support itself may affect positively the Co sulfide properties, for example by increasing the electron-deficient character of the Co sulfide, resulting in a longer distance between Co and S. Obviously more information about the relation between acidity and activity and the effect on the local (electronic) structure is necessary to discriminate between these suggestions. Activity tests of Co(GPA)CaY or Co(GPA)HY with different ion exchange degrees of $Na^+$ (so with different acidity) could give valuable information.

## CONCLUSION

The presence of protons in zeolite-supported metal sulfides has several implications. First, the protons anchor the quasi-atomically dispersed metal sulfide species in the zeolite pores. Unfortunately, when contacted with a base the interaction is broken and migration to, followed by sintering at, the external surface occurs. Second, the protons change the catalytic properties of the metal sulfide. A higher acidity provides a more active catalyst in thiophene HDS. Third, a strong interaction results in a protolysis reaction that adversely affects the catalytic performance. However, the protolysis can be partially prevented by blocking the cation sites in the sodalite cages.

## ACKNOWLEDGMENTS

These investigations have been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Technology Foundation (STW). The research has been performed under the auspices of NIOK, the Netherlands Institute for Catalysis Research, Lab Report TUE-99-6-01. The authors thank Mr. E. M. van Oers and Dr. P. J. Kooyman (National Centre of High Resolution Electron Microscopy, Delft University of Technology) for conducting sulfur analysis and TEM measurements, respectively. TPS measurements were carried out at the Delft University of Technology with the assistance of Dr. H. R. Reinhoudt and Dr. A. D. van Langeveld.

## REFERENCES

1. Minderhoud, J. K., and van Veen, J. A. R., *Fuel Processing Technology* **35**, 87 (1993).
2. Welters, W. J. J., de Beer, V. H. J., and van Santen, R. A., *Appl. Catal. A* **119**, 253 (1994).
3. Vissenberg, M. J., de Bont, P. W., Arnouts, J. W. C., van de Ven, L. J. M., de Haan, J. W., van der Kraan, A. M., de Beer, V. H. J., van Veen, J. A. R., and van Santen, R. A., *Catal. Lett.* **47**, 155 (1997).
4. Cid, R., Orellana, F., and López Agudo, A., *Appl. Catal.* **32**, 327 (1987).
5. Laniecki, M., and Zmierczak, W., *Zeolites* **11**, 18 (1991).
6. Laniecki, M., and Zmierczak, W., *in* "Zeolite Chemistry and Catalysis" (P. A. Jacobs *et al.*, Eds.), Vol. 69, p. 331. Elsevier, Amsterdam, 1991.
7. Welters, W. J. J., Vorbeck, G., Zandbergen, H. W., de Haan, J. W., de Beer, V. H. J., and van Santen, R. A., *J. Catal.* **150**, 155 (1994).
8. Breysse, M., Cattenot, M., Kougionas, V., Lavalley, J. C., Mauge, F., Portefaix, J. L., and Zotin, J. L., *J. Catal.* **168**, 143 (1997).
9. Mojet, B. L., Ph.D. thesis, Utrecht University, Utrecht, The Netherlands, 1997.
10. Zhang, Z., Lerner, B., Lei, G.-D., and Sachtler, W. M. H., *J. Catal.* **140**, 481 (1993).
11. de Bont, P. W., Vissenberg, M. J., Boellaard, E., van Santen, R. A., de Beer, V. H. J., and van der Kraan, A. M., *Bull. Soc. Chim. Belg.* **104**, 205 (1995).
12. de Bont, P. W., Vissenberg, M. J., Boellaard, E., van Santen, R. A., de Beer, V. H. J., van Veen, J. A. R., and van der Kraan, A. M., "Conference Proceedings ICAME-95" (I. Ortalli, Ed.), Vol. 50, p. 649. SIF, Bologna, 1996.
13. Vissenberg, M. J., de Bont, P. W., van Oers, E. M., de Haan, R. A., Boellaard, E., van der Kraan, A. M., de Beer, V. H. J., and van Santen, R. A., *Catal. Lett.* **40**, 25 (1996).
14. Dendooven, E., Mortier, W. J., and Uytterhoeven, J. B., *J. Phys. Chem.* **88**, 1916 (1984).
15. Okamoto, Y., *Catal. Today* **39**, 45 (1997).
16. Okamoto, Y., and Katsuyama, H., *Ceram. Process.* **43**, 2809 (1997).
17. Duchet, J. C., van Oers, E. M., de Beer, V. H. J., and Prins, R., *J. Catal.* **80**, 86 (1983).
18. Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93**, 813 (1984).
19. Scheffer, B., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 18 (1990).
20. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
21. de Bont, P. W., Vissenberg, M. J., Boellaard, E., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., and van der Kraan, A. M., *Hyperfine Interact.* **111**, 39 (1998).
22. de Bont, P. W., Vissenberg, M. J., Boellaard, E., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., and van der Kraan, A. M., *J. Phys. Chem. B* **101**, 3072 (1997).
23. de Bont, P. W., Vissenberg, M. J., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., and van der Kraan, A. M., *J. Phys. Chem. B* **102**, 5876 (1998).
24. de Bont, P. W., Vissenberg, M. J., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., and van der Kraan, A.M., submitted for publication.
25. Nørskov, J. K., Clausen, B. S., and Topsøe, H., *Catal. Lett.* **13**, 1 (1992).
26. Wiegand, B. C., and Friend, C. M., *Chem. Rev.* **92**, 491 (1992).
27. Smit, T. S., and Johnson, K. H., *Catal. Lett.* **28**, 361 (1994).
28. Hensen, E. J. M., Vissenberg, M. J., de Beer, V. H. J., van Veen, J. A. R., and van Santen, R. A., *J. Catal.* **163**, 429 (1996).
29. Crajé, M. W. J., Ph.D. thesis, Interfacultair Reactor Instituut, Delft University of Technology, Delft, The Netherlands, 1992.
30. Hensen, E. J. M., Ph.D. thesis, Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands, to be published.