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Instability of zeolite Y supported cobalt sulfide hydrotreating catalysts in the absence of H_2S

M.J. Vissenberg, P.W. de Bont [a], E.M. van Oers, R.A. de Haan, E. Boellaard [a], A.M. van der Kraan [a], V.H.J. de Beer and R.A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[a] *Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands*

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Ion exchanged CoNaY was sulfided at 473 and 673 K and subsequently heated in He at 673 and 773 K. The resulting samples were characterized by means of overall sulfur analysis, temperature programmed Ar treatment and Fourier transform infrared spectroscopy. It was shown that during He flushing at sufficiently high temperature a protolysis reaction occurs resulting in the decomposition of Co sulfide into Co^{2+} ions and H_2S.

Keywords: ion exchanged CoNaY zeolite; sulfidation; protolysis; overall sulfur analysis; temperature programmed Ar treatment; Fourier transform infrared spectroscopy

1. Introduction

Small metal sulfide particles have attractive properties for hydrotreating reactions. Carbon supported Co sulfide is known to have a high activity for thiophene hydrodesulfurization (HDS) [1,2]. This high activity was explained by the formation of small Co sulfide particles. In situ ^{57}Co Mössbauer emission spectroscopy (MES) and extended X-ray absorption fine structure (EXAFS) proved to be useful characterization techniques to study the influence of the sulfidation procedure on the particle size of Co sulfide supported on carbon and alumina [3–7]. To study more closely the influence of particle size on thiophene HDS zeolites provide an interesting support material due to their well-defined pore structure. For example, Y-type zeolite is composed of hexagonal prisms, sodalite cages and supercages with maximum entrances of 2.6, 2.6 and 7.4 Å and diameters of 2.6, 6.6 and 11.8 Å, respectively.

The preparation of zeolite supported metal sulfides consists of two steps. First the zeolite is loaded with a metal, and second the metal is transformed into a metal sulfide. Both steps have a large influence on the dispersion (particle size) and distribution (in- or outside the zeolite pores) of the metal sulfide. Amongst others, Welters et al. [8] found that the use of impregnation results in an inhomogeneous distribution of the metal over the zeolite. A large part of the metal was found on the exterior of the zeolite. Ion exchange resulted in homogeneous well-dispersed metal ions in the zeolite pores. Also, the sulfidation step has a large influence on the catalyst. Zeolite NaY contains about 25 wt% physisorbed water. De Bont et al. [9] have shown that, after sulfidation of ion exchanged CoNaY in the presence of physisorbed water, large and/or well-ordered "Co sulfide" species (Co_9S_8 like) were formed. Sulfidation of dehydrated CoNaY resulted in the formation of small "Co sulfide" species. Preliminary results of HREM analysis suggest that these species are located in the zeolite cavities. A similar behavior was reported earlier [8] for NiNaY. By combined high resolution electron microscopy (HREM), Xe adsorption and ^{129}Xe NMR measurements, it was shown that the large nickel sulfide particles were located at the external zeolite surface, while the small nickel sulfide particles were distributed over the zeolite cavities [8].

In the case of small Co sulfide particles embedded in the zeolite the following phenomenon was observed. When H_2S was replaced by an inert gas (He, N_2 or Ar) at 673 K the color of the catalyst gradually changed from black to grayish blue. In a previous paper the results of a MES study on this behavior were presented [10]. The present paper deals with a more detailed study of this phenomenon. Sulfided dehydrated CoNaY was treated with He at different temperatures. The initial sulfur content and thermal stability of the Co sulfide species were determined by conventional chemical sulfur analysis and temperature programmed Ar treatment, respectively. Fourier transform infrared (FTIR) was used to study changes in location (cation site) of Co.

2. Experimental

2.1. Preparation

CoNaY (8 wt% Co) was prepared by ion exchange of NaY (AKZO, $Na_{55}(AlO_2)_{55}(SiO_2)_{137}$) with a 1 M solution of $CoCl_2$ (Merck) followed by washing and drying in air (16 h, 383 K).

CoNaY was heated to 673 K in He (6 K/min, 60 ml/min) to dehydrate the zeolite, cooled (when necessary) in He flow and sulfided in situ at 473 or 673 K for 2 h in 10% H_2S/H_2 (60 ml/min). Subsequently, the sulfided samples were flushed in He at different temperatures (60 ml/min, 2 h at 673 K or 72 h at 773 K) and some of them were resulfided (473 or 673 K) after this treatment. The samples will be denoted as follows: CoNaY (S x K, He y K, S′ z K) with x, y and z standing for sulfidation temperature, He treatment temperature and resulfidation temperature, respectively. All samples prepared are presented in table 1.

2.2. *Cobalt and sulfur analysis*

For sulfur analysis, all Co species (unsulfided and sulfided) present in the sample 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 analyzed by AAS and the amount of sulfate was determined by titration with barium perchlorate. In order to remove physisorbed H_2S, the freshly (re)sulfided samples (CoNaY (S 473 K), CoNaY(S 673 K), CoNaY (S 473 K, He 773 K, S′ 473 K) and CoNaY (S 673 K, He 673 K, S′ 673 K)) were flushed in He at 298 K for 2 h prior to sulfur analysis.

2.3. *Temperature programmed Ar treatment*

Temperature programmed Ar treatment was carried out in an in situ temperature programmed sulfidation facility which has been described elsewhere [11,12]. The measurements were carried out according to the following procedure. CoNaY (300 mg) was heated in Ar (60 ml/min, 6 K/min, from 298 to 673 K, 2 h at 673 K) for dehydration. After cooling to room temperature Ar was replaced by $H_2S/H_2/Ar$ (3.3%, 28.1%, 68.6%, 60 ml/min) and the sample was sulfided (60 ml/min, 6 K/min, from 298 to 673 K, 2 h at 673 K), cooled to room temperature and flushed in Ar (60 ml/min) till no H_2S was measured at the reactor outlet. Subsequently, the sample was heated to 1273 K at a rate of 6 K/min and the H_2S concentration at the reactor outlet was measured by a UV spectrophotometer at 195 nm during the complete treatment. For comparison, also a carbon supported Co sulfide sample was measured.

2.4. *Fourier transform infrared spectroscopy (FTIR)*

IR spectra of two different samples were recorded using a Bruker IFS 113v FTIR spectrometer equipped with a heatable cell connected to a vacuum system. The samples were pretreated according to the procedure described in the preparation section and transferred – in short contact with air – to the IR cell. Spectra were recorded at 300 K after additional dehydration of the samples at 723 K in vacuum for 15 h.

3. Results

3.1. *Color and sulfur analysis*

In table 1 the colors of the samples and the S/Co ratios after various treatments at different temperatures are given. Two observations were made. First, when the sample sulfided at 673 K was treated in He at 673 K a color change from black to grayish blue was observed and simultaneous the S/Co ratio decreased from 0.8 to 0.2 (compare samples 2 and 3). Second, the samples sulfided at 473 and 673 K showed a different behavior upon He treatment at 673 K for 2 h. CoNaY (S 673 K) turned into grayish blue (compare samples 2 and 3) while CoNaY (S 473 K) stayed black (compare samples 6 and 7) although again the S/Co decreased strongly. A higher temperature (773 K) and a longer flushing time (72 h) were required to cause a color change for CoNaY (S 473 K) albeit that in this case the color did not change from black to grayish blue but to purple (compare samples 6 and 8), which is the same color as that of the dehydrated

Table 1
Color and S/Co ratio of CoNaY after different treatments

Sample		Color	S/Co ratio
number	treatment		
1	CoNaY (He 673 K)	purple	n.a.
2	CoNaY (S 673 K) [a]	black	0.8
3	CoNaY (S 673 K, He 673 K)	grayish blue	0.2
4	CoNaY (S 673 K, He 773 K) [b]	grayish blue	0.2
5	CoNaY (S 673 K, He 673 K, S′ 673 K) [a]	black	0.6
6	CoNaY (S 473 K) [a]	black	0.9
7	CoNaY (S 473 K, He 673 K)	black	0.1
8	CoNaY (S 473 K, He 773 K) [b]	purple	0.0
9	CoNaY (S 473 K, He 773 K, S′ 473 K) [a]	black	0.5

[a] Prior to sulfur analysis the samples are flushed for 2 h at 298 K in He.
[b] These samples are flushed for 72 h in He.

precursor (sample 1). Also the behavior towards sulfur removal (changes of the S/Co ratio) was different. CoNaY (S 673 K, He 673 K) still contained 0.2 sulfur atoms per Co atom. This ratio did not change after a more severe He treatment at 773 K for 72 h (see sample 4). On the other hand, CoNaY (S 473 K, He 773 K) lost all its sulfur (sample 8).

Resulfidation caused the samples CoNaY (S 673 K, He 673) and CoNaY (S 473 K, He 773 K) to regain their original black colors. It also led to an increase of the S/Co ratio, although the ratio found after the first sulfidation was not reached (compare samples 2 and 5, samples 6 and 9).

3.2. *Temperature programmed Ar treatment*

Fig. 1 shows the temperature dependence of the H_2S concentration as measured by UV spectroscopy at 195 nm during heating of CoNaY (S 673 K) and Co/carbon (S 673 K) in Ar. For sulfided CoNaY desorption of physisorbed H_2S was detected between 330 and 400 K and around 723 K production of H_2S was observed. Five different in situ sulfided CoNaY (S 673 K) samples were measured. They all showed a color change from black to grayish blue and on two occasions a small amount of elemental sulfur has been formed. Sulfided Co/carbon showed no significant H_2S release at all.

3.3. *Fourier transform infrared spectroscopy (FTIR)*

The far IR spectra obtained for the purple CoNaY (He 673 K) sample and the grayish blue CoNaY (S 673 K, He 673 K) sample are presented in fig. 2. Both spectra showed the same vibration modes. Since the spectra were not recorded from one and the same sample it was difficult to analyze the spectra quantitatively. In the far IR region (40–340 cm^{-1}) cation vibrations are observed. Jacobs et al. [13] studied infrared vibration modes of monovalent and divalent cations, including Co^{2+}, in ion exchanged zeolite Y. Based on their findings, the bands observed at 102 and 173 cm^{-1} are assigned to Co^{2+} located at site I′ and site I respectively. The vibration mode at 144 cm^{-1} is assigned to Co^{2+} cations in sodalite cages (site II′). The broad band at 195 cm^{-1} is due to sodium at site II. The vibration modes between 280 and 350 cm^{-1} are lattice vibrations.

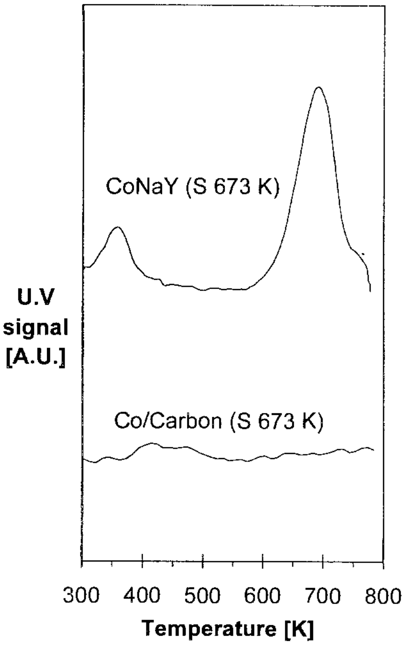

Fig. 1. Temperature programmed Ar treatment pattern for sulfided CoNaY and Co/carbon. A negative peak means consumption of H_2S, and a positive peak means desorption.

4. Discussion

Treating sulfided CoNaY (S 673 K) with He at 673 K has the following result. The freshly sulfided sample (see sample 2) is black and the S/Co ratio close to the thermodynamically stable form (Co_9S_8). During He treatment at 673 K the color of the sample changes and the S/Co ratio decreases (compare samples 2 and 3). This indicates that Co sulfide decomposes.

Three possible Co sulfide decomposition reactions are shown in fig. 3. It is important to notice that the zeolite is loaded with Co^{2+} by means of ion exchange. The Co^{2+} ions are present as charge compensation for the negatively charged zeolite framework. During sulfidation small neutral Co sulfide species are formed and the charge compensation is taken over by protons [14]. As proposed in fig. 3 these protons may react under certain conditions with the small cobalt sulfide species to form Co^{2+} and H_2S (reaction a) or Co^{2+}, S_x and H_2 (reaction b). This type of proton induced reactions which can be referred to as protolysis has already been described for oxidation of Pt^0 and Ni^0 in NaY [15,16] and for decomposition of NaY supported CdS in Cd^{2+} and H_2S [14].

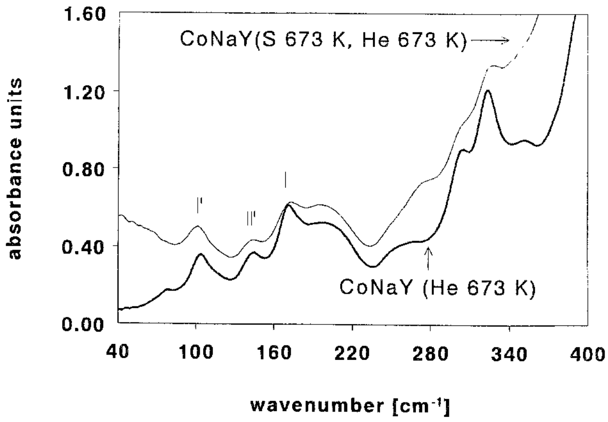

Fig. 2. Fourier transform infrared spectra of CoNaY (He 673 K) and CoNaY (S 673 K, He 673 K).

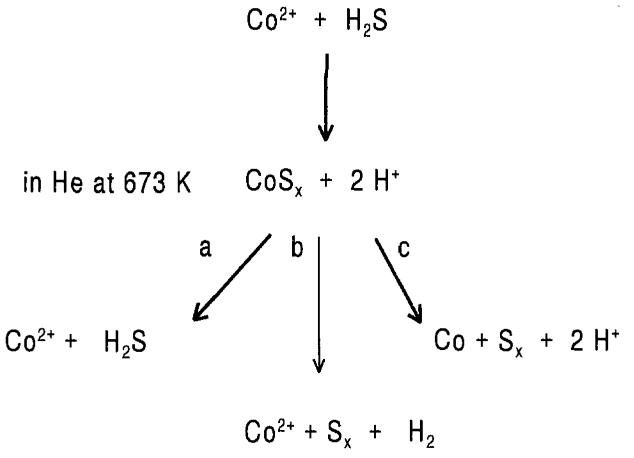

Fig. 3. Possible reactions that explain loss of sulfur during He treatment.

However, in our experiments besides H_2S formation also deposition of elemental sulfur was sometimes observed during the color change. The formation of elemental sulfur can be explained by reactions (b) and (c) differing in the role of the protons. In reaction (b), Co sulfide is oxidized by protons under formation of elemental sulfur, Co^{2+} ions, and hydrogen. In reaction (c), however, protons do not react and Co sulfide decomposes into metallic Co and elemental sulfur.

Temperature programmed Ar treatment (referred to as Ar-TPT) was used to distinguish between the formation of H_2S (reaction (a)) or elemental sulfur (reactions (b) and (c)). The Ar-TPT pattern of the zeolite supported Co sulfide (fig. 1) shows production of H_2S around 723 K, while for the carbon supported Co sulfide sample no H_2S production is observed. Even during temperature programmed reduction in 67% H_2/Ar of Co sulfide supported on alumina no production of H_2S was observed around this temperature [17]. An essential difference between carbon, alumina and ion exchanged zeolite supported metal sulfide catalysts is the presence of protons in the zeolite support which can cause protolysis reactions [14–16]. Therefore, H_2S is most probably formed by protolysis of the Co sulfide (reaction (a)).

In the case of CoNaY, it was not possible to quantify accurately the degree of sulfidation since the zeolite adsorbs a large excess of H_2S, of which only a small part is consumed for sulfidation. For this reason S/Co ratios could only be obtained by overall sulfur analysis.

Sometimes, deposition of elemental sulfur was observed during Ar-TPT. The formation of elemental sulfur can be explained by reactions (b) and (c). During Ar-TPT the H_2 concentration was monitored by means of a thermal conductivity detector. No production of hydrogen could be detected implying that at most only a small amount of H_2 could be formed. So, reaction (b) does not look relevant.

In order to estimate the relevance of reaction (c) the state of Co (metallic Co, Co sulfide or charge compensating Co^{2+} ion) was determined by MES [10]. From the MES spectra it could be deduced that the spectral contribution of the "Co sulfide" species decreased during the He treatment, and that the spectral contribution of the high-spin Co^{2+} nearly reached the value of the fresh dried sample. The presence of a small amount of highly dispersed (superparamagnetic) metallic Co cannot be excluded, as its spectral contribution (single line) will be hidden in the spectrum at about 0 mm/s. However, the strong increase of the spectral contribution of high spin Co^{2+} by the He treatment is in line with the result (occurring of reaction (a)) of Ar-TPT. Furthermore, the occurrence of reaction (c) to a significant extent can be excluded.

IR provides information about the position of Co^{2+} ions in the zeolite. The IR spectra indicate that in CoNaY (S 673 K, He 673 K) the formed Co^{2+} ions occupy the same positions as in the dehydrated precursor. It is known [18] that Co^{2+} ions preferably occupy site I, I′, and II′ after dehydration. According to Jacobs et al. [13], the IR spectrum of dehydrated CoNaY is in agreement with this occupation. The neutral Co sulfide entities formed during sulfidation will not have a strong interaction with the zeolite lattice and it can be expected that the vibration modes of cations will be absent in the spectrum. Since the IR cell is not H_2S resistant the sulfided sample could not be measured. From the results obtained by other techniques (MES, EXAFS, HREM, thiophene HDS activities, Xe adsorption measurements and ^{129}Xe NMR [9,19]) it is reasonable to assume that the Co sulfide is located as very small particles in the supercages. The same vibration modes as in the dehydrated sample are observed after He treatment. This indicates that the Co^{2+} ions formed during the He treatment move back to the preferred cation sites.

In summary, during He treatment of sulfided CoNaY at 673 K a protolysis reaction occurs resulting in decomposition of Co sulfide into H_2S and Co^{2+} ions occupying the same cation positions as in dehydrated CoNaY.

The difference in color after He treatment of 473 and 673 K sulfided samples is remarkable (table 1, samples 3 and 8). CoNaY (S 473 K, He 773 K) had the same purple color as the dehydrated unsulfided sample (CoNaY (He 673 K)) (compare samples 1 and 8). This was to be expected because the results described above indicate that during He treatment of CoNaY (S 473 K) all sulfur was removed and the dry precursor state is restored (compare samples 6 and 8). The grayish blue color of CoNaY (S 673 K, He 673 K) and CoNaY (S 673 K, He 773 K) (samples 3 and 4) indicates that something different happened. In addition, 0.2 atom sulfur per atom Co was found in these samples. It is possible that the grayish blue color is due to the formation of a sulfur compound like the one in the ultramarine mineral, where S_3^- radicals in sodalite cages are causing the blue color [20]. However, preliminary EXAFS results indicate that after

He treatment the surrounding of Co by oxygen increases but also some Co remains surrounded by sulfur. This suggests that the grayish blue color is caused by tetrahedrally coordinated Co. Further research will be carried out to clarify the color variance induced by the increase of the sulfidation temperature from 473 to 673 K.

The effect of resulfiding CoNaY (S 473 K, He 773 K) at 473 K is distinctly different from the completely reversible sulfidation–desulfidation behavior suggested by Herron et al. [14] for sulfided CdNaY. From the results of sulfur analysis (table 1) on a resulfided CoNaY (S 473 K, He 773 K, S′ 473 K) sample it follows that the sulfidation–desulfidation reaction is only partially reversible. The S/Co ratio of CoNaY (S 473 K, He 773 K, S' 473 K) is considerably lower than that of CoNaY (S 473 K) (compare samples 6 and 9). Possibly, a redistribution of Co^{2+} ions occurs during He treatment at 773 K in such a way that a larger part of Co^{2+} ions occupies cation sites (e.g. site I) inaccessible for H_2S.

The Co sulfide protolysis reaction as described in this paper seems a more general phenomenon for ion exchanged NaY supported metal sulfides. Herron et al. [14] observed this reaction for sulfided ion exchanged CdNaY. In addition, we have obtained results (Ar-TPT, sulfur analysis and color change) indicating that protolysis also occurs in sulfided ion exchanged NiNaY albeit that more rigorous conditions (higher temperature (773–1073 K) and/or longer flushing times (168 h at 773 K)) are required. Therefore, it is reasonable to assume that other acidic zeolite supported metal sulfides are also susceptible to protolysis. This reaction which leads to a breaking up of the zeolite encaged small metal sulfide particles might be avoided by adjusting the application conditions of this type of catalysts or by avoiding proton formation during catalyst preparation for instance via the use of carbonyl complexes as practiced by several authors [21–26].

5. Conclusion

When supported on ion exchanged NaY (instead of alumina, silica or carbon) Co sulfide is unstable under relatively mild conditions. The small cobalt sulfide particles present in the supercages react with the zeolite protons (protolysis) resulting in the formation of H_2S and reoccupation of cation sites by Co^{2+} ions.

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