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

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The influence of the sulfidation temperature of dehydrated ion exchanged CoNaY on the catalytic activity and structure was studied by thiophene HDS activity measurements, overall sulfur analysis, temperature programmed sulfidation, Xe adsorption measurements in combination with ^{129}Xe NMR, EXAFS and ESR. It was shown that up to a sulfidation temperature of 573 K small highly active Co sulfide clusters were formed in the supercages. Sulfidation above 573 K led to decomposition of these Co sulfide particles by a protolysis reaction resulting in the formation of H_2S and a blue colored Co compound having almost no HDS activity.

Keywords: ion exchanged CoNaY zeolite, protolysis, sulfur analysis, temperature programmed sulfidation, EXAFS, ESR, ^{129}Xe NMR, thiophene hydrodesulfurization

1. Introduction

Recently, we have shown that Co sulfide in ion exchanged type CoNaY decomposes in Co^{2+} and H_2S when heated in helium [1,2]. It appeared that this decomposition was caused by a reaction of the Co sulfide with the charge compensating protons formed during sulfidation ($Co^{2+} + H_2S \rightarrow CoS_x + 2H^+$). This type of proton induced reaction which can be referred to as protolysis was described earlier for oxidation of Pt^0 and Ni^0 in NaY [3,4] and for decomposition of NaY supported CdS [5]. In our previous studies it was observed that the temperature at which CoNaY was sulfided influenced the extent of the protolysis reaction during He treatment [2]. In addition, the sulfidation temperature also affected the structure and thiophene hydrodesulfurization (HDS) activity [6]. The present paper deals with a more detailed study on the influence of the sulfidation temperature on the structure and thiophene HDS activity of NaY supported Co sulfide catalysts (CoNaY) prepared via ion exchange (4, 5.4 and 8 wt% Co) and in situ sulfidation in 10% H_2S/H_2 after dehydration. The (quasi) in situ structural characterization techniques applied include: overall sulfur analysis, temperature programmed sulfidation (TPS), Xe adsorption combined with ^{129}Xe NMR, HREM/EDX, EXAFS and ESR. Thiophene HDS activity was measured in a microflow reactor at 1 bar and 673 K.

2. Experimental

2.1. Preparation

CoNaY catalysts (4, 5.4 or 8 wt% Co, calculated on the basis of water free zeolite) were prepared by ion exchange of 10 g NaY (AKZO, $Na_{55}(AlO_2)_{55}(SiO_2)_{137}$, containing 25 wt% physisorbed water) with 250 ml of 0.02, 0.03 or 1 M solutions of $CoCl_2$ (Merck) followed by washing until Cl^- free and drying in air at 383 K for 16 h.

The sulfidation of CoNaY was carried out as follows. The samples 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 373 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 will be denoted as follows: Co(x)NaY(dehydrated) and Co(x)NaY(y h, z K) with x, y and z standing for wt% Co, sulfidation time and sulfidation temperature, respectively. One sample [Co(4)NaY(2 h, 773 K, 2 h 673 K)] was sulfided at 673 K for 2 h after sulfidation at 773 K for 2 h.

2.2. Cobalt and 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 [2]. 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.

2.3. Temperature programmed sulfidation (TPS)

The TPS facility has been described elsewhere [7,8].

The experiment was carried out according to the following procedure. Co(8)NaY (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 773 K, 2 h at 773 K). The H_2S concentration in the reactor outlet was measured by a UV spectrophotometer at 195 nm during the complete treatment.

2.4. Thiophene hydrodesulfurization (HDS)

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). Catalyst samples of 200 mg Co(4)NaY (particle size between 125 and 425 μm, containing 25 wt% physisorbed water) were dehydrated and sulfided in situ according to the procedure described in the preparation section. When necessary, the samples were heated or cooled 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 is 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 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_{hds}) assuming the reaction to be first order in thiophene [9]. In view of the rapid deactivation due to the coke formation only initial activities (after 2 min reaction time) were compared.

2.5. Xe adsorption measurements in combination with ^{129}Xe NMR

The (presulfided) samples viz. Co(8)NaY (dehydrated), Co(8)NaY(2 h, 473 K) and Co(8)NaY (2 h, 773 K) were transferred into the NMR tubes using a recirculation type glovebox (O_2 and H_2O content lower than 2 ppm), evacuated at 303 K to a pressure below 10^{-2} Pa and stored in a volumetric adsorption apparatus. Xe is adsorbed at 303 K at different Xe pressures. The NMR spectra of the adsorbed Xe were recorded at the same temperature on a Bruker MSL 400 Fourier transform instrument at 110.7 MHz with pulse excitation (0.5 s pulse delay) on stationary samples. The number of scans varied between 10^3 and 6×10^4.

2.6. Extended X-ray absorption fine structure (EXAFS)

A Co(4)NaY(2h, 773 K) sample was pressed in a self-supporting wafer and mounted in an EXAFS cell using a glove box. The thickness of this wafer was chosen such that the absorption μx is about 2.5 to give an optimal signal to noise ratio in the EXAFS spectrum. The EXAFS spectrum at the Co K-edge was measured up to $k = 12.5$ Å^{-1} at EXAFS station 8.1 of the SRS in Daresbury (UK).

2.7. Electron spin resonance spectroscopy (ESR)

The (presulfided) samples viz. Co(8)NaY (dehydrated), Co(8)NaY(2 h, 673 K) and Co(8)NaY (2 h, 773 K) were supplied in sealed ampuls to Dr. M. Hartman (University of Houston) for ESR measurements at 15 K.

3. Results and discussion

The color and the S/Co ratio of the three CoNaY (4, 5.4 and 8 wt%) samples sulfided at various temperatures are given in table 1. A striking influence of the sulfidation temperature on these parameters was observed. The color changed from black to blue and the S/Co ratio decreased with increasing sulfidation temperature. Both phenomena were not reversible. As was shown earlier [1,2], heating of sulfided ion exchanged CoNaY in He above 723 K induced a protolysis reaction resulting in the formation of H_2S and a color change from black to grayish blue. In order to check whether the sulfur loss and color change observed during sulfidation in 10% H_2S/H_2 could also be caused by the formation of H_2S due to a protolysis type reaction, TPS measurements were carried out. The TPS pattern of Co(8)NaY (dehydrated) is given in figure 1. Four peaks can be distinguished. The first (large negative) peak is caused by H_2S adsorption (physisorption and chemisorption) during the isothermal period at 298 K. The second (large positive) peak with maximum at 340 K and the third (small negative) peak with minimum at 585 K reflect the overall result of desorption of (excess) H_2S and H_2S uptake required for Co sulfide formation, respectively. In this respect it is relevant to note that the results of a Mössbauer emission spectroscopy (MES) study on the sulfidation of ion exchanged Co(4)NaY showed that the sulfidation started at 300 K and ceased around 673 K [6]. In addition, Inamura et al. [10] found by TPS that the sulfidation of silica supported CoO (10 wt%) is completed at 600 K. The fourth peak in the TPS pattern

Table 1
Color and S/Co ratio after 2 h sulfidation at different temperatures

Sample sulfidation temp. (K)	Color	S/Co		
		Co(4)NaY	Co(5.4)NaY	Co(8)NaY
473	black	0.90	n.a.	0.88
673	black	0.75	n.a.	0.82
773	blue	0.65	0.48	0.37

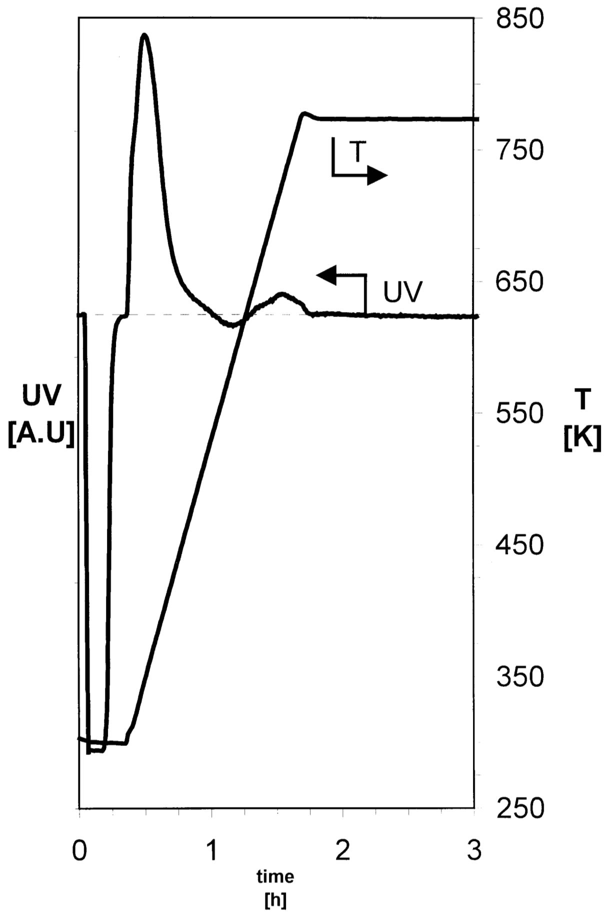

Figure 1. TPS pattern of Co(8)NaY. A negative peak means H_2S consumption/adsorption, a positive peak means production/desorption.

(maximum at 723 K) is due to H_2S production and coincides with a color change from black to blue which is not observed during sulfidation of alumina [11] or silica [10] supported CoO. Interestingly, during temperature programmed Ar treatment of sulfided ion exchanged Co(8)NaY(2 h, 673 K) a H_2S production peak and a color change were observed at the same temperature whereas carbon supported Co sulfide did not show such a peak [2]. Since the latter peak could be ascribed to protolysis of Co sulfide, it is concluded that the same holds for the 723 K peak present in the TPS pattern.

The protolysis reaction had a large impact on the thiophene HDS activity. Figure 2 shows the relation between initial reaction rate constant and sulfidation temperature. Sulfidation up to 573 K resulted in very high initial activities. Above 573 K the activity strongly decreased with increasing sulfidation temperature and reached a very low constant level at 723–773 K. The HDS activity could not be restored by resulfidation at 473 K. So, the protolysis reaction led to a blue catalyst having almost no HDS activity.

The decrease in activity after sulfidation above 573 K, when the catalyst is still black, can also be explained by protolysis. Table 2 lists for various temperatures the sulfidation time required to realize a color change from black to blue. Clearly, the protolysis reaction started above 573 K but the standard 2 h sulfidation time applied for activity measurements was not sufficient for complete protolysis at 623 and 673 K. Figure 2 shows that when the sulfidation time at 673 K was increased the catalytic activity further decreased. This implies that Co(4)NaY(2 h, 623 K) and Co(4)NaY(2 h, 673 K) contained besides black not decomposed Co sulfide species also blue colored Co species. After 20 h sulfidation at 673 K the decomposition was completed and the catalyst had the same blue color and very low activity as the catalysts sulfided at 723 and 773 K.

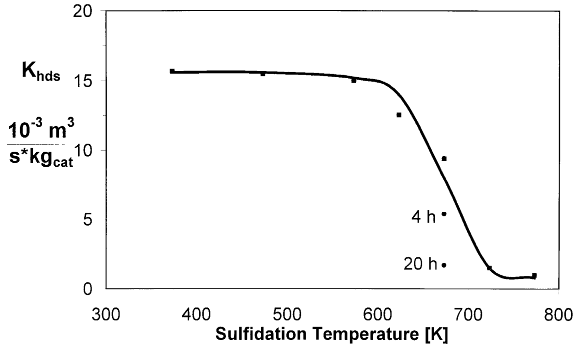

Figure 2. Initial thiophene HDS activity of Co(4)NaY as function of sulfidation temperature and time.

The above deactivation phenomenon suggests that the blue Co species are inactive, possibly because they are inaccessible for thiophene (i.e. they are located in the hexagonal prisms and/or sodalite cages). The maximum entrance of these cavities is 2.6 Å which is smaller than the size of thiophene.

Xe adsorption measurements combined with ^{129}Xe NMR show that the blue species are inaccessible for Xe. The adsorption capacities of Co(8)NaY(dehydrated), Co(8)NaY(2 h, 473 K) and Co(8)NaY(2 h, s 773 K) are essentially the same. The chemical shift as a function of amount of adsorbed Xe is depicted in figure 3. For Co(8)NaY(dehydrated) one signal was found at low Xe pressures versus two signals at higher Xe pressures. Bonardet et al. [12,13]. showed that the chemical shift and shape of the plot are strongly affected by the extent of dehydration. They ascribed the signal with the small

Table 2
Sulfidation time required to realize a color change for Co(8)NaY from black to blue at different temperatures

Sulfidation temp. (K)	Sulfidation time (h)
773	0.5
723	1.5
673	8.0
623	80
573	> 170 [a]

[a] Even after 170 h sulfidation no color change was observed.

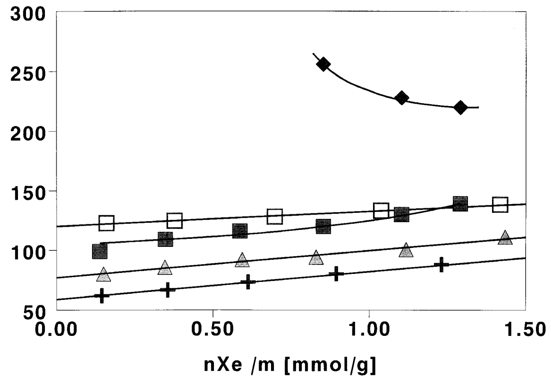

Figure 3. ^{129}Xe-NMR chemical shift versus the amount of adsorbed Xe for (+) NaY, (■) Co(8)NaY(dehydrated) first signal, (◆) Co(8)NaY(dehydrated) second signal, (□) Co(8)NaY(2 h, 473 K), (▲) Co(8)NaY(2 h, 773 K).

chemical shift to Xe in CoNaY dehydrated to an extent of 95% (approximately 13 H_2O per unit cell is left) and the signal with the large chemical shift to Xe in fully dehydrated CoNaY. The presence of two signals points to a slow exchange of Xe and can only be explained by the presence of two kinds of particles with different pore sizes. In the case of particles with different pore sizes, Xe will adsorb preferentially in the particle with the smaller pores, while at higher Xe loading also the particles with the larger pores will be occupied [14,15]. The free space of the pores containing fully dehydrated Co is larger than those containing 95% dehydrated Co, hence at low Xe pressures only the signal of 95% dehydrated Co is found while at higher Xe pressures also the signal of fully dehydrated Co appears. The chemical shift of Xe in contact with fully dehydrated Co is larger than the chemical shift of 95% dehydrated Co because of the shielding by water in the latter case. The presence of more than one NMR signal suggests that the sample is not homogeneously dehydrated. Most probably the dehydration in a He flow is less effective than static dehydration in vacuum. In a NMR study on $Mo(CO)_6$NaY [16] differences were also found between samples dehydrated in a He flow or in vacuum.

The chemical shift of ^{129}Xe in Co(8)NaY(2 h, 473 K) was much higher than that of ^{129}Xe in NaY. This can be explained by an interaction between Xe and Co sulfide located in the supercages resulting in a longer residence time of the Xe in these zeolite cavities and consequently in an increased chemical shift [17]. The increase in sulfidation temperature from 473 to 773 K resulted in a strong decrease of the ^{129}Xe chemical shift. However, the chemical shift of ^{129}Xe in Co(8)NaY(2 h, 773 K) remained higher than for NaY. This might very well be caused by a (relatively weak) interaction between Xe and Co in the sodalite cages as reported by Bornadet et al [12] for dehydrated CoNaY.

Also, the EXAFS results (FT functions) obtained for, Co(4)NaY(dehydrated), Co(4)NaY(2 h, 673 K) [6,18] and Co(4)NaY(2 h, 773 K) and shown in figure 4 indicated that with increasing sulfidation temperature the formed Co sulfide in NaY decomposed and a redistribution of the Co species occurred. Upon dehydration, Co^{2+} ions in ion exchanged CoNaY occupy zeolite cation positions [19]. This effect is reflected in the presence of the second backscattering peak (Co–Si contribution at 3.25 Å) in the FT-function of Co(4)NaY (dehydrated). After sulfidation at 673 K this second backscattering peak disappeared while the first peak changed from an oxygen contribution to a sulfur contribution ($N_{\text{Co–S}} = 5.2$, $R_{\text{Co–S}} = 2.23$ Å) with a small oxygen contribution ($N_{\text{Co–O}} = 0.2$, $R_{\text{Co–O}} = 1.90$ Å). However, after sulfidation at 773 K the second backscattering peak (Co–Si contribution) re-appeared while the sulfur contribution in the first peak decreased. From the relative shift to the right of the first backscattering peak in Co(4)NaY(2 h, 773 K) compared to CoNaY (dehydrated) it can be concluded that a small Co–S contribution remained after sulfidation at 773 K. In addition, a large increase of the white line (raw data, not shown) was observed after sulfidation at 773 K indicating the presence of a Co–O interaction. Therefore, the first strong peak is composed of a Co–O and a Co–S contribution. Due to interference between these contributions and the presence of the second strong backscattering peak (Co–Si) the exact S coordination number and its distance is difficult to determine (The $N_{\text{Co–S}}$ depends on the coordination distance chosen). The Co–S coordination is about 1.3 when its distance is fixed at 2.29 Å and the Co–O contribution turned out to be $N_{\text{Co–O}} = 2.5$, $R_{\text{Co–O}} = 2.02$ Å. These results can be explained by decomposition of Co sulfide and migration of the formed Co species to the cation positions.

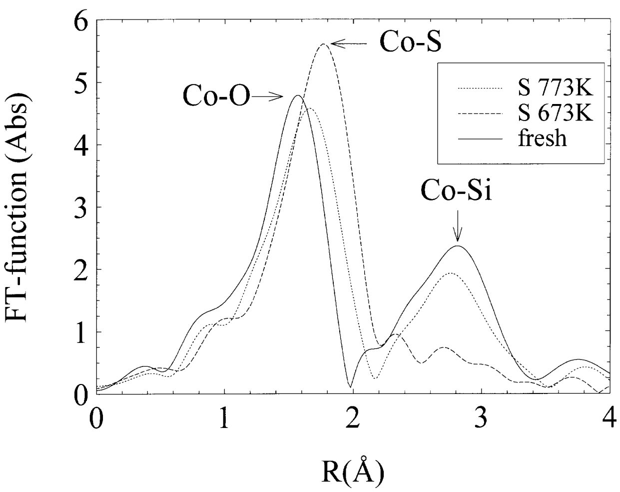

Figure 4. EXAFS FT function (k^3) for Co(4)NaY(dehydrated), Co(4)NaY(2 h, 673 K) and Co(4)NaY(2 h, 773 K).

At first sight the location of Co species in 773 K sulfided CoNaY and the parent dehydrated CoNaY looks similar. However, these two samples were distinctly different in several respects. (I) Co(8)NaY(dehydrated) was purple, even after dehydration at 773 K, while Co(8)NaY(2 h, 773 K) was blue. (II) The blue sample had a remarkably high stability in the HREM beam suggesting that the Co species are strongly bonded to the lattice. For most monovalent and higher valent cations no stabilizing effect on the zeolite lattice was found [20]. (III) The linear ^{129}Xe chemical shift plot shown in figure 3 for Co(8)NaY(2 h, 773 K) indicates that the Co cations are shielded (by oxygen and/or sulfur atoms) whereas that is not the case for dehydrated CoNaY [12]. (IV) After protolysis the blue Co(8)NaY(2 h, 773 K) sample still contained sulfur (table 1). In addition, sulfur analysis on 773 K sulfided CoNaY samples containing 4, 5.4 or 8 wt% Co showed that although the S/Co ratio decreased with increasing Co content (table 1) all samples contained about 5 S atoms per NaY unit cell. The possibility that the blue color of these samples was caused by the presence of S_3^- and S_2^- radicals in sodalite cages as described for the mineral ultramarine [21] was checked by ESR. In the event, a signal at $g \approx 2$, ascribable to the presence of sulfur radicals in ultramarine [21] was not observed (figure 5). (V) Dehydrated Co(8)NaY contained tetrahedrally coordinated Co^{2+} as can be concluded from the presence of a signal at $g \approx 6$ in figure 5 [22]. Sulfidation for 2 h at 673 K resulted in a very strong (about 96%) decrease of this Co tetrahedral signal. Interestingly, after sulfidation at 773 K the blue decomposed sample showed no Co ESR signal indicating the formation of a non paramagnetic Co compound. It should be noted that the sharp but weak signal at $g \approx 4$ in this spectrum is due to the presence of a very small amount of Fe in the parent NaY. (VI) Upon resulfiding of Co(4)NaY(2 h, 773 K) at 673 K the EXAFS spectrum hardly changed (figure 6). This is in clear contrast with the changes observed when Co(4)NaY(dehydrated) was sulfided at 673 K. The Co species present in Co(4)NaY (dehydrated) are reactive towards H_2S, whereas those present in Co(4)NaY (2 h, 773 K) are not.

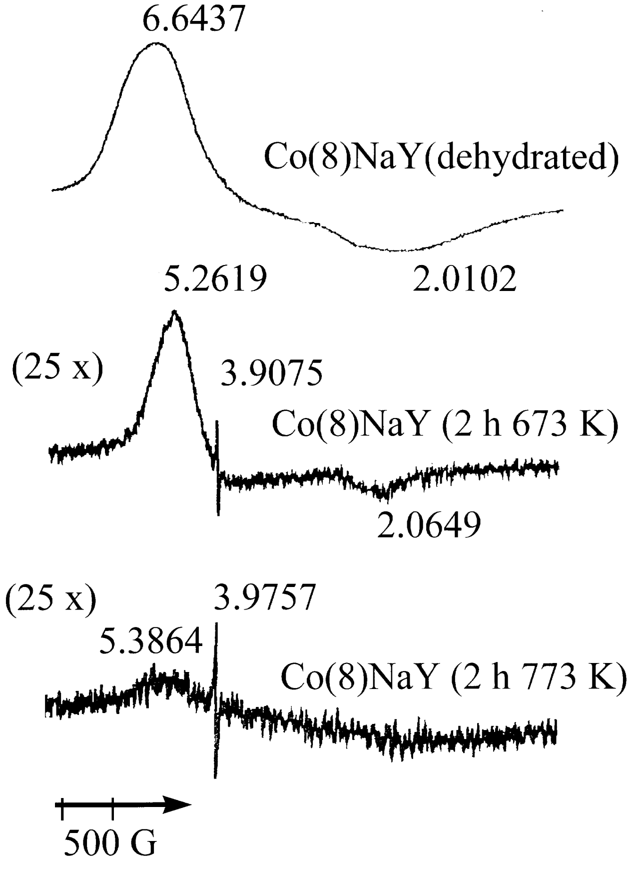

Figure 5. ESR spectra of Co(8)NaY(dehydrated), Co(8)NaY(2 h, 673 K) and Co(8)NaY(2 h, 773 K).

The above mentioned differences between CoNaY(dehydrated) and CoNaY(2 h, 773 K) suggest that the latter contains Co species which are positioned in the sodalite cages (^{129}Xe NMR, inaccessibility for thiophene and H_2S), strongly interacting with the zeolite lattice (HREM) where they are tetrahedrally coordinated (blue color not caused by sulfur radicals) by oxygen and/or sulfur (EXAFS, fixed S content per unit cell irrespective of Co content). For a more refined description of the blue Co species further information for instance on the location of Co with respect to the zeolite lattice and the nature/location of the sulfur is required.

4. Conclusion

Small Co sulfide particles present in the supercages of ion exchanged NaY are not stable in a 10% H_2S/H_2 atmosphere above 573 K. This Co sulfide instability is most likely caused by a protolysis type reaction with the charge compensating NaY protons (initially formed during sulfidation: $Co^{2+} + H_2S \rightarrow CoS_x + 2H^+$) resulting in the formation of H_2S and Co species causing the

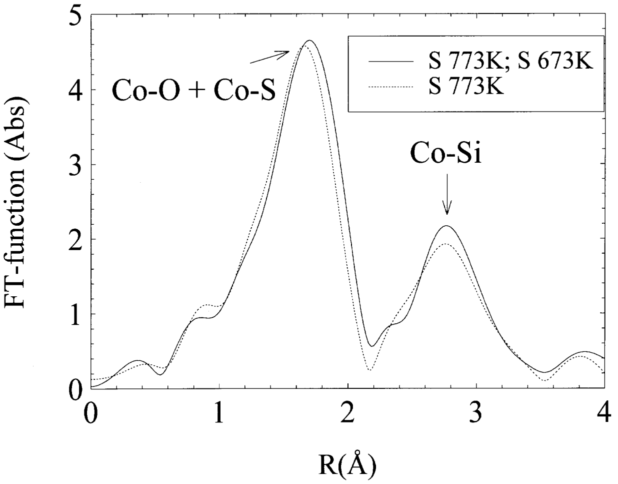

Figure 6. EXAFS FT function (k^3) of Co(4)NaY(2 h, 773 K) and Co(4)NaY(2 h, 773 K; 2 h, 673 K).

blue color. The blue colored Co-species are clearly different from the purple colored Co^{2+} ions in dehydrated CoNaY showing that the protolysis reaction is not simply the reversed reaction of sulfidation.

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