Influence of Water on the Sulfidation of Co/NaY and Co/CaY Prepared by Impregnation. A Mössbauer Emission Spectroscopy and EXAFS Study

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The influence of physisorbed water on the sulfidation of impregnation type Co/NaY(imp) and Co/CaY(imp) catalysts which contain about 4 wt % Co and are prepared via pore volume impregnation is studied by Mössbauer emission spectroscopy and extended X-ray absorption fine structure. It is found that in the absence as well as in the presence of water, sulfidation of the impregnated samples finally results in the formation of Co_9S_8-like species at the outer zeolite surface. In the presence of water, this process proceeds via the intermediate formation of a well-ordered "CoS_{1+x}" phase (NiAs structure). Water removal prior to sulfidation retards the formation of Co_9S_8-like species. This retardation in Co_9S_8 formation is found to be more effective for CaY−zeolite than for NaY−zeolite, which means that a larger part of the formed "Co−sulfide" is preserved in highly dispersed "Co-sulfide" particles. These findings are clearly different from those obtained earlier with ion exchanged CoNaY(ion ex) samples, for which drying prior to sulfidation resulted in very small "Co−sulfide" species with no resemblance to "Co_9S_8".

Introduction

The hydrocracking process is designed to produce high yields of middle distillate products and often consists of two separate stages. The first stage is a hydrotreatment step using a sulfur-resistant catalyst for the removal of for instance sulfur (HDS) and nitrogen (HDN) and the mild hydrogenation of aromatic structures. In the second stage the actual hydrocracking occurs, using a catalyst which combines hydrogenation (metal sites) and cracking (acidic sites) functions. Metal−sulfide particles in acidic zeolites provide the possibility to combine these two stages in one catalytic system.

As the catalytic activity will be correlated with the dispersion of the active phase, an attendant advantage of using zeolites is that they have a well-defined three-dimensional pore system which creates the possibility to prepare catalysts containing very small uniformly shaped metal sulfide particles inside the zeolite cavities. For this reason, these catalyst systems are interesting not only for their potential application in hydrocracking processes but also for checking the relevance of a structural model for "Co−sulfide" species present in conventional Co−Mo sulfide based hydrotreating catalysts as proposed by Crajé et al.[2] This model predicts among other things a relation between particle size and/or ordering of these Co−sulfide species and a parameter viz. the quadrupole splitting (QS) measured by means of Mössbauer emission spectroscopy (MES).

Although stabilized Y (USY) zeolites are most commonly used for industrial hydrocracking,[3] the original NaY zeolite is used as support for our model catalysts in order to avoid changes in catalytic properties, dispersion or degree of sulfidation of the metal sulfide phase caused by the extra framework alumina and the mesopores present in the stabilized Y zeolite.[4] To study the formation of the small metal−sulfide particles inside the zeolite, it is necessary to apply in situ techniques. MES[5−10]

and extended X-ray absorption fine structure (EXAFS)[11,12] and especially the combination of both[2,13] have proven their usefulness in studies of carbon- and alumina-supported cobalt−sulfide particles.

Recently we have shown that physisorbed water (20−25 wt %) present in ion exchanged CoNaY(ion ex) (containing about 4 wt % Co) has a strong influence on the formation of Co-sulfide particles in this Y-type zeolite.[1] It was found by MES, EXAFS, and thiophene HDS that sulfidation of a carefully dried ion-exchanged CoNaY(ion ex) results in the formation of small and highly active Co−sulfide species. However, when the physisorbed water has not been removed prior to sulfidation, much larger and better ordered Co_9S_8 species having a relatively low activity were observed. The present paper describes the results of catalysts prepared via impregnation. As sulfidation of ion-exchange type CoNaY(ion ex) will create strong Brønsted acidity[14,15] and sulfidation of impregnation type Co/NaY(imp) will not,[16] an impregnation type Co catalyst supported on already acidic CaY (Co/CaY(imp)) is also included in the present study.

Experimental Section

Catalyst Preparation. A NaY−zeolite (ZI, $Na_{53}(AlO_2)_{53}$-$(SiO_2)_{139} \cdot x H_2O$) and a CaY−zeolite are used as supports. The CaY support is prepared by repeated ion exchange of NaY with aqueous $CaCl_2$ solutions followed by washing until Cl^--free.

MES samples are prepared by pore volume impregnation of the two different zeolites with aqueous solutions of $CoCl_2$ (Merck p.a.), to which about 34 Mbq [57]Co as aqueous solution of $CoCl_2 \cdot 6H_2O$ (Cynge) is added. Each catalyst sample contains about 300 mg of wet zeolite (containing 25 wt % of physisorbed water) and is directly prepared in a sample holder, which can be used for the Mössbauer emission spectroscopy measurements. The following four samples were prepared: Co(4.0)/NaY(imp), Co(4.5)/NaY(imp), Co(3.8)/CaY(imp), and Co(4.6)/CaY(imp). The numbers between parentheses represent the weight percentages Co which are calculated on the basis of the water-free zeolite from the amount of cobalt present in the impregnation

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solutions. After impregnation, all samples are dried overnight in static air at 383 K and stored in ambient air. For the EXAFS measurements a second Co(4.0)/NaY(imp) batch (without [57]Co) is prepared in the same way.

In the following, the impregnation type samples are denoted by Co/NaY(imp) and Co/CaY(imp). The ion-exchange sample (studied earlier[1] and used here as reference sample) will be denoted by CoNaY(ion ex).

Catalyst Treatment. To study with MES the influence of the physisorbed water on the sulfidation of the impregnated catalysts, they are all exposed to various temperature and gas treatments indicated by [gas, z K, 1 h + y h]. This notation stands for a linear temperature increase in a certain gas flow during 1 h up to z K followed by an isothermal period at z K for y hours. Each sample is cooled to room temperature in the same gas flow and kept under this gas atmosphere. All subsequent treatments have been performed in situ in a Mössbauer reactor.

First, all catalysts are calcined [air, 673 K, 1 h + 2 h] and subsequently kept in ambient air to become saturated with water. Co(4.0)/NaY(imp) and Co(3.8)/CaY(imp) are used as prepared and are referred to as wet Co/NaY(imp) and Co/CaY(imp). To remove the physisorbed water Co(4.5)/NaY(imp) and Co(4.6)/CaY(imp) are subjected to an additional drying procedure [He, 673 K, 1 h + 2 h]. The duration of this drying procedure is checked to be sufficient on a separate wet catalyst sample. They are referred to as dry Co/NaY(imp) and Co/CaY(imp).

The wet as well as the dry catalysts are stepwise sulfided in a 10 vol % H_2S/H_2 gas mixture [H_2S, z K, 1 h + 1 h] at the following (z K) temperatures 300, 373, 473, 573, and 673 K. After each sulfiding step a MES spectrum is recorded at room temperature in the 10 vol % H_2S/H_2 atmosphere.

The two dry Co(4.0)/NaY(imp) EXAFS samples are calcined and dried in the same way as the MES samples. They are stepwise sulfided up to either 473 or 673 K and stored in sealed glass ampules via a recirculation type glovebox (O_2 and H_2O content below 2 ppm).

For convenience sake, in the following paragraphs the information between brackets such as (fresh) or (z K) added at the end of the catalyst notation, indicates that the catalyst is measured in the fresh, i.e., non-sulfided state (for example, wet Co/NaY(imp,fresh)) or after a sulfidation treatment at a temperature of z K (for example, dry Co/NaY(imp,z K)).

Techniques. All sample treatments are carried out in an in situ reactor, which has been described elsewhere.[17] The heating section as well as the outer container are made of stainless steel, and furthermore, the reactor was placed horizontally. This makes it possible to measure in situ the Mössbauer emission spectrum after each sulfidation step or gas treatment.

The spectra are recorded at room temperature using a constant acceleration spectrometer in a triangular mode with a single-line absorber of $K_4Fe(CN)_6 \cdot 3H_2O$ enriched in [57]Fe. The velocity scale was calibrated by using a SNP ($Na_2(Fe(CN)_5NO) \cdot 2H_2O$) absorber and a [57]Co:Rh source. Positive velocities correspond to the absorber moving away from the source and the zero of the velocity scale is relative to the single-line position of the $K_4Fe(CN)_6 \cdot 3H_2O$ absorber measured with [57]Co:Rh.

The spectra are fitted with calculated subspectra consisting of Lorentzian-shaped lines. The line widths (Γ) and the absorption areas of the constituent peaks of the quadrupole doublets are constrained to be equal.

The ampules with the sulfided EXAFS samples are opened in a glovebox in which the dry Co/NaY(imp,473 K) and Co/NaY(imp,673 K) samples are pressed in self-supporting wafers with an optimal thickness which gives an absorption μx of about 2.5. The wafers are mounted in vacuum-tight sample holders

within the glovebox and the spectra are measured (quasi) in situ at liquid N_2 temperature using EXAFS-station 8.1 of the SRS in Daresbury. The storage ring was operated at 2.0 GeV, the ring current was in the range 180−250 mA. The Si(220) monochromator was detuned to 70% intensity to remove higher harmonics in the X-ray beam. Three scans are recorded for each treatment. All the data manipulation and analyses are done with the XDAP program version 2.0.3.[20] The EXAFS oscillations in k space are obtained from the X-ray absorption spectra by subtracting a victoreen curve followed by a cubic spline background removal.[21] Normalization is done by division by the step height of the edge. For the analysis of the spectra, phase shifts and backscattering amplitudes from reference compounds are used. For the Co−S reference the coordination in CoS_2 is measured at station 8.1. It is an octahedral coordination of Co by S at a distance of 2.315 Å.[22] The Ni−Ni coordination in NiO is used[23] as a Co−Co reference.

Transmission electron microscopy (TEM) is performed using a Philips CM 30 ST electron microscope with a field emission gun as the source of electrons operated at 300 kV. The sulfided samples are mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in n-hexane on the grid, followed by drying at ambient conditions in an Ar glovebox. The samples are transported to the microscope using a special vacuum transfer specimen holder.

Results

Sulfidation of Wet and Dry Co/NaY(imp) Studied by MES. In Figure 1 the room-temperature Mössbauer spectra of the stepwise sulfided wet and dry Co/NaY(imp) catalysts are presented. It is clear that the spectral shape is changing at increasing sulfidation temperature. Both samples behave distinctly different during the various sulfidation steps, especially during those carried out at relatively low temperatures. The sulfidation behavior of wet Co/NaY(imp) is more or less comparable with that observed earlier in the 473−673 K sulfiding temperature range for wet CoNaY(ion ex).[1] However, the dry Co/NaY(imp) spectra are completely different from those recorded earlier for dry CoNaY(ion ex).[1]

The MES spectra were decomposed using a similar set of two quadrupole doublets as applied before[1] (only the spectrum of wet Co/NaY(imp,673 K) consists of one doublet). Due to the low resolution of the very broad absorption lines there was in the first instance no need to increase the number of doublets in the analyzing procedure. The quantitative result for the quadrupole splittings (QS) of the Co−sulfide doublets of dry and wet Co/NaY(imp) is shown in Figure 2. It clearly shows a different behavior for both catalysts. The gradually decreasing QS value of dry Co/NaY(imp) reflects the growth and/or ordering of Co−sulfide particles. The rather high QS value for dry Co/NaY(imp,473 K) (0.81 mm/s) suggests the presence of only very small particles. However, this is not confirmed by HREM measurements which show some rather large Co−sulfide particles present at the outer zeolite surface. Furthermore, it turned out that for dry Co/NaY(imp,673 K) the number of such large Co−sulfide particles on the outer zeolite surface was strongly increased. As with HREM still the presence of small Co−sulfide particles inside the cavities of the NaY−zeolite cannot be excluded and with MES most probably an "averaged" QS value for the Co−sulfide particles will be determined in the above given analyzing procedure, we decided to analyze the dry Co/NaY(imp,473−673 K) MES spectra with two different doublets for the Co−sulfide spectral contribution. One contribution representing the more structured Co_9S_8 phase
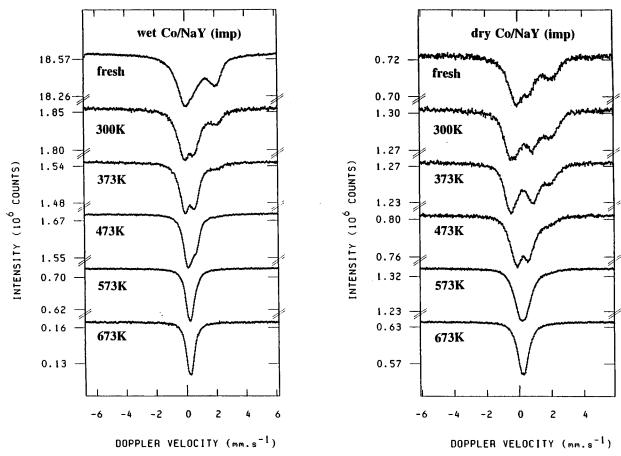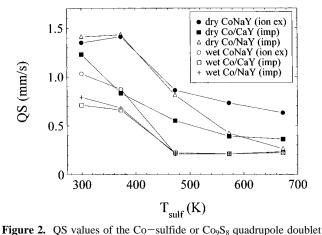
Figure 1. MES spectra of wet and dry Co/NaY(imp) (fresh and sulfided at 300, 373, 473, 573, and 673 K).

Figure 2. QS values of the Co−sulfide or Co_9S_8 quadrupole doublet (IS = 0.19−0.27 mm/s) in wet and dry Co/NaY(imp), Co/CaY(imp) and CoNaY(ion ex) upon increasing sulfidation temperature. The presented QS values for dry Co/NaY and dry Co/CaY are the averaged QS values of all cobalt−sulfide species present.

(isomer shift: IS = 0.22 mm/s, QS = 0.26 mm/s), the other one a Co−sulfide phase with a higher QS value. The thus gathered quantitative results of the spectral analyses are presented in Table 1 (the QS value of the dry impregnated catalysts presented in Figure 2 can now be considered as an average of the Co_9S_8 and Co−sulfide QS values).

As shown in Table 1 "sulfidation" at 300 K appears to have a different effect on the wet and dry catalysts. In the case of wet Co/NaY(imp,300 K) the spectral contribution of the doublet with Isomer Shift (IS $\approx$ 0.27 mm/s) is increased while its QS value is decreased, from 0.91 to 0.79 mm/s. For dry Co/NaY-(imp,300 K) the QS of this doublet is increased from 0.94 to 1.41 mm/s while its spectral contribution remained constant.

On the basis of the findings by Crajé et al.[2,8−10] the spectral contribution with an IS between 0.19 and 0.27 mm/s has been assigned to Co−sulfide species. (However, observations based on color changes show that most likely the Co−sulfide doublet for dry Co/NaY(imp,300 K) is not due to a sulfidic component.) Although the corresponding QS value is decreased with increasing sulfidation temperature for wet Co/NaY(imp) as well as dry Co/NaY(imp) the course of this decrease is different. For wet Co/NaY(imp) the QS value of the Co−sulfide species declines rapidly to the value observed for Co_9S_8[5] after sulfidation at 473 K and stays more or less constant at higher sulfidation temperatures, whereas for dry Co/NaY(imp) after sulfidation at 473 K two different phases of the Co−sulfide species are present. One phase with a relatively high QS value the other one with the QS value of 0.26 mm/s of Co_9S_8.[5] Additionally, with increasing sulfidation temperature the spectral amount of Co_9S_8 increases.

The spectral contribution with an IS between 0.81 and 1.07 mm/s is assigned to a high-spin Co^{2+} doublet and is indicative for the presence of a cobalt−oxygen interaction. This contribution disappears for wet Co/NaY(imp) already after sulfidation at 473 K, but for dry Co/NaY(imp) only after the final sulfidation step at 673 K, indicating a difference in the cobalt−oxygen interaction strength in the wet and dry Co/NaY(imp) catalysts.

As already mentioned, at sulfidation temperatures higher than 373 K the QS value of the Co−sulfide spectral contribution of wet Co/NaY(imp) decreases to the value of a Co_9S_8-like phase (QS = 0.26 mm/s[5]). However, the spectrum of wet Co/NaY-(imp,473 K) shows an additional doublet (IS = 0.36 mm/s, QS = 0.68 mm/s, A = 52%). A similar contribution has also been found for wet CoNaY(ion ex)[1] (IS = 0.35 mm/s, QS = 0.67 mm/s, A = 48%) and can be ascribed to CoS_{1+x} (0.06 $\leq$ x $\leq$ 0.18) following Topsøe et al.[5] (The MES parameters of CoS_{1+x}

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TABLE 1: MES Parameters of Wet and Dry Co/NaY(imp) after Successive Sulfidation Steps[a]

	Co−oxygen				Co−sulfide				Co$_9$S$_8$				CoS$_{1+x}$				high-spin 2+			
T_s (K)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)
							Wet Co(4.0)/NaY(imp)													
fresh	0.27	0.91	1.40	50													1.04	1.97	0.96	50
300					0.25	0.79	0.93	71									1.07	2.01	0.95	29
373					0.27	0.68	0.75	89									1.02	2.18	0.75	11
473									0.26	0.21	0.63	48	0.36	0.68	0.54	52				
573									0.26	0.21	0.53	91	0.39	0.73	0.38	9				
673									0.25	0.23	0.49	100								
							Dry Co(4.5)/NaY(imp)													
fresh	0.26	0.94	1.00	55													1.04	2.06	1.05	45
300					0.19	1.41	0.91	53									0.96	2.08	1.05	47
373					0.19	1.43	0.83	64									0.88	2.13	0.98	36
473					0.24	0.81	0.83	80	0.24[b]	0.26[b]	0.36	2					0.81	2.00	0.92	18
573					0.26	0.81	0.75	53	0.24[b]	0.26[b]	0.49	40					0.81	1.92	0.78	7
673					0.30	0.79	0.72	24	0.24	0.25	0.52	76								

[a] Isomer shift: IS ± 0.03 mm/s; quadrupole splitting: QS ± 0.03 mm/s; line width: Γ ± 0.05 mm/s; spectral contribution: A ± 5%. Co$_9$S$_8$: IS = 0.26 mm/s; QS = 0.26 mm/s.[5] CoS$_{1+x}$: IS = 0.42 mm/s; QS = 0.61 mm/s.[5] [b] Fixed during fit.
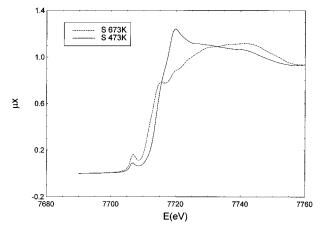

Figure 3. XANES region of dry Co/NaY(imp) (sulfided at 473 and 673 K).

are presented in the legend of Table 1.) The CoS$_{1+x}$ has the NiAs structure with the cobalt atoms octahedrally surrounded by sulfur.[18] Interestingly, the spectral contribution (A) of the CoS$_{1+x}$ in the wet Co/NaY(imp,473 K) sample is 52% which is clearly higher than the 11% of the high-spin 2+ component present after sulfidation at 373 K. This difference in spectral contributions strongly suggests that CoS$_{1+x}$ cannot be a simple transition state between the high-spin 2+ and the Co-sulfide species. The CoS$_{1+x}$ disappears with increasing sulfidation temperature and after a sulfidation treatment at 673 K only the Co$_9$S$_8$-like phase remains.

The dry Co/NaY(imp) displays a different behavior upon sulfidation. The spectral contribution (A) of the doublet assigned to Co−sulfide species is gradually decreasing after sulfidation above 373 K in favor of a spectral contribution assigned to Co$_9$S$_8$ species (IS = 0.24; QS = 0.26 mm/s). However, after sulfidation at 673 K still a contribution with a relatively high QS value is present. Furthermore, there is no indication for the formation of the "intermediate" CoS$_{1+x}$ phase as in the case of the wet Co/NaY(imp) sample. The high-spin 2+ spectral contribution gradually decreases with increasing sulfidation temperature and has disappeared at 673 K.

Sulfidation of Dry Co/NaY(imp) Studied by EXAFS. Since the detectors are equipped with Kapton windows the EXAFS spectra of the dry sulfided (473 and 673 K) Co/NaY-(imp) samples could be measured up to a k value of 14 Å^{-1}.

The Co−K edges (the XANES -region) are shown in Figure 3. The edge shape changes upon increasing sulfidation temperature. Both spectra exhibit a large pre-edge peak which is caused by the 1s → 3d transition. Only in the case where Co

is perfectly octahedral or trigonal prismatic surrounded no pre-edge peak will be observed.[12,19] So, the pre-edge peak present in Figure 3 indicates a coordination number lower than six in the first coordination shell for both samples. In addition, the absorption edge is shifted to lower energies upon increasing sulfidation temperature. For CoNaY(ion ex) this "chemical" shift is correlated with the difference in oxidation state and is found to be 3 eV going from the fresh to the completely sulfided state (unpublished result). In Figure 3 the "chemical" shift has a value of about 1.7 eV indicating still the presence of a Co−O interaction after sulfidation at 473 K. After sulfidation at 673 K this interaction has vanished completely as shown by the disappearing of the white line. This result is in line with the MES-results showing that after sulfidation at 473 K still a high-spin 2+ contribution is found in the spectrum which has vanished after sulfidation at 673 K.

In Figure 4 the k^3-weighted χ and FT functions (absolute value and imaginary part) are presented. It is clear that the signal-to-noise ratio for both spectra are high. Both catalysts display a total different χ and FT function. The amplitude of the χ function increases upon increasing sulfidation temperature and also the phase is shifted. The amplitude increase indicates that upon increasing sulfidation temperature the Co species are going from a more or less disordered system to a much better ordered one. The χ function of Co/NaY(imp,673 K) shows some "beat nodes" in the amplitude envelope, whereas Co/NaY(imp,473 K) has a smooth envelope. This indicates contributions of atoms at well-defined different distances from the Co atom after sulfidation at 673 K.
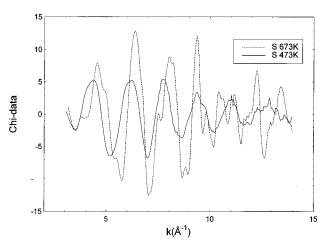
The FT spectra provide more structural information. First, the FT spectrum of Co/NaY(imp,473 K) (Figure 4b) shows no significant contributions beyond 4 Å in contrast with the Co/NaY(imp,673 K) spectrum where large contributions beyond 6 Å are observed. Second, the main peak of Co/NaY(imp,673 K) is very broad and certainly consists of at least two backscatterers. Third, the second peak has a large amplitude in the case of Co/NaY(imp,673 K), but is hardly present for Co/NaY(imp,473 K).

Both EXAFS spectra are analyzed using the analysis program XDAP version 2.0.3.[20] The spectra are fitted in r space until a reasonable good fit is obtained for k^1- and k^3-weighted spectra in k space and r space. As the FT range for Co/NaY(imp,473 K) 3.10−12.12 Å^{-1} and for Co/NaY(imp,673 K) 3.23−12.42 Å^{-1} is used. The ranges for the r fit have been kept between 0.6 and 4.2 Å. The deduced EXAFS parameters are given in Table 2.

TABLE 2: EXAFS Parameters of Dry Co/NaY(imp) after Sulfidation at 473 and 673 K[a]

T_{sulf} (K)	Co–O				Co–S				Co–Co				Co–Co			
	N	R (Å)	$\Delta\sigma^2$ (Å²)	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å²)	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å²)	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å²)	ΔE_0 (eV)
473	0.2	1.91	−0.0007	6.7	5.0	2.29	0.0025	1.7	1.8	2.99	0.0088	−9.6				
673					5.8	2.21	0.0018	−0.1	2.9	2.54	0.0048	−20.5	1.9	3.46	0.0000	2.5
					0.8	2.36	−0.0078	−4.3					4.3	3.57	0.0054	−16.8

a Co$_9$S$_8$:Co(t)–S: $R = 2.13$ Å, $N = 1$, and $R = 2.23$ Å, $N = 3$; Co(o)–S: $R = 2.36$ Å, $N = 6$; Co(t)–Co(t): $R = 2.51$ Å, $N = 3$. Co(t)–Co(t): $R = 3.47$ Å, $N = 3$, and $R = 3.54$, $N = 3$ (t and o denote a tetrahedral and an octahedral cobalt atom, respectively).[25]
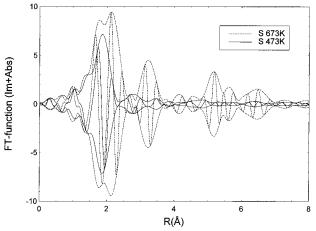

Figure 4. (a, top) K^3-weighted χ-functions of dry Co/NaY(imp) (sulfided at 473 and 673 K). (b, bottom) K^3-weighted FT functions (Abs + Im) of dry Co/NaY(imp) (sulfided at 473 and 673 K).

After sulfidation at 473 K still a small Co–O contribution is found. Although it is possible to produce several good fits of the spectrum with other parameter sets for the O contribution, these different parameters do not influence the two main Co–S and Co–Co contributions. These last two contributions are found at much larger distances as reported by Bouwens et al.[24] for Co$_9$S$_8$. They are more or less comparable with those observed by Crajé et al.[12] for sulfided Co/C. After sulfidation at higher temperatures the contributions are changing. Due to measuring over a larger energy range, the spectrum of Co/NaY-(imp,673 K) has a higher resolution than the Co$_9$S$_8$ spectrum published by Bouwens et al.[24] It turned out to be impossible to fit the first main peak in our spectrum with a Co contribution (at 2.55 Å) and a S contribution (at 2.22 Å) as used by Bouwens et al.[24] (only by limiting the FT range to 4.0−10.0 Å^{-1}, we were able to analyze the spectrum of Co/NaY(imp,673 K) with one S contribution at 2.22 Å and one Co contribution at 2.55 Å). Therefore, the *S* contribution is split into two (of which the *R* parameters are kept fixed), resulting in a reasonable good fit and a similar procedure has been used for the Co–Co contribution in the second main peak. After sulfidation at 673 K the results are more or less in agreement with the crystal-

lographic parameters of Co$_9$S$_8$[25] (see Table 2). Although trying to identify the contributions beyond a distance of 4 Å is meaningless, it can be concluded from the presence of these contributions that the formed Co$_9$S$_8$ must have a high degree of crystallinity.

Sulfidation of Wet and Dry Co/CaY(imp) Studied by MES. The MES spectra obtained for stepwise sulfided wet and dry Co/CaY(imp) are presented in Figure 5. The numerical results of the spectral analysis are presented in Table 3. The shape of the spectra of both catalysts is clearly changing at increasing sulfidation temperature. From the spectral changes it is evident that sulfidation starts already at 300 K.

The sulfidation behavior of wet Co/CaY(imp) is comparable with that of wet Co/NaY(imp), as can be concluded from the similarity of the fitting results (compare Tables 1 and 3). Also dry Co/CaY(imp) behaves more or less comparable with dry Co/NaY(imp) as shown by the simplest fitting results (the "averaged" quadrupole splitting) of the Co−sulfide doublet as presented in Figure 2.

The more detailed analysis of the dry Co/CaY(imp) MES spectra using two different doublets for Co−sulfide (Co$_9$S$_8$ and highly dispersed Co−sulfide) as explained before in the case of Co/NaY(imp) shows that the spectral contribution (A) of the doublet assigned to Co−sulfide species is gradually decreasing with increasing sulfidation temperature in favor of a spectral contribution assigned to Co$_9$S$_8$ species (IS = 0.24, QS = 0.26 mm/s). However, after sulfidation at 673 K a higher spectral contribution of Co−sulfide (QS ≈ 0.80 mm/s) is present for dry Co/CaY(imp) (40%) than for dry Co/NaY(imp) (24%) (see Tables 1 and 3).

Analysis of the dry Co/CaY(imp,573 K and 673 K) spectra turned out to be rather difficult, due to a broad high-spin 2+ spectral component. It appeared to be possible to analyze this component in several ways leading to different combinations of IS and QS values. However, these different analyses of the high-spin 2+ contribution did not influence the QS value of the Co−sulfide doublet. Therefore, we have chosen in Table 3 those fitting results which are the best in line with those obtained for the high-spin 2+ contribution at lower sulfidation temperatures.

Discussion

The phenomenon of a decreasing QS value of the Co−sulfide species with increasing sulfidation temperature as shown in Tables 1 and 3, was observed before by Crajé et al.[8−10,13] in MES studies on the sulfidation of carbon- and alumina-supported Co and CoMo catalysts. Combining this variation in QS values and the coordination parameters deduced from EXAFS,[12,13] Crajé et al.[2] proposed a structural model for the Co−sulfide species. In this model, the Co−sulfide species (characterized by a doublet with a varying QS value depending on, e.g., the presence of Mo, sulfidation temperature, Co loading[9]) is a highly dispersed particle characterized by its *size* and *ordering*. The *particle size* indicates the number of Co atoms that is associated with a Co−sulfide particle, while the Co−sulfide is said to be more *ordered* the better its coordination parameters agree with those of Co$_9$S$_8$. Furthermore, a decreasing QS value reflects

Sulfidation of Co/NaY and Co/CaY

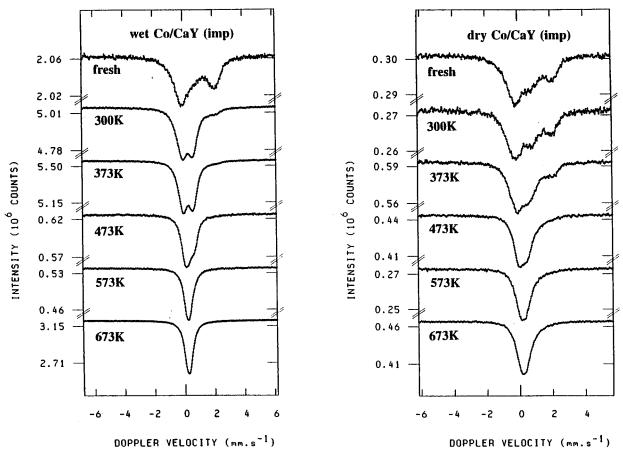*J. Phys. Chem. B, Vol. 101, No. 16, 1997* **3077**

Figure 5. MES spectra of wet and dry Co/CaY(imp) (fresh and sulfided at 300, 373, 473, 573, and 673 K).

TABLE 3: MES Parameters of Wet and Dry Co/CaY(imp) after Succesive Sulfidation Steps[a]

T_s (K)	Co−oxygen IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	Co−sulfide IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	Co$_9$S$_8$ IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	CoS$_{1+x}$ IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)	high-spin 2+ IS (mm/s)	QS (mm/s)	Γ (mm/s)	A (%)
							Wet Co(3.8)/CaY(imp)													
fresh	0.27	1.02	1.41	44													1.02	2.17	0.95	56
300					0.28	0.71	0.81	90									1.02[b]	2.29	0.88	10
373					0.28	0.66	0.70	98									1.04[b]	2.10[b]	0.51	2
473									0.26	0.22	0.59	49	0.36	0.70	0.53	51				
573									0.25	0.21	0.50	88	0.35[b]	0.67[b]	0.57	12				
673									0.25	0.22	0.52	100								
							Dry Co(4.6)/CaY(imp)													
fresh	0.26	1.16	1.31	64													0.99	2.19	0.88	36
300					0.23	1.34	1.01	55	0.24[b]	0.26[b]	0.87	9					0.96	2.12	0.85	36
373					0.25	1.05	0.98	61	0.24[b]	0.26[b]	0.77	18					0.94	2.16	0.77	21
473					0.25	0.75	0.72	64	0.24[b]	0.26[b]	0.52	25					0.87[b]	1.77	0.68	11
573					0.25	0.75	0.68	46	0.22	0.26[b]	0.46	42					0.87[b]	1.54[b]	1.17	12
673					0.27	0.80	0.73	40	0.22	0.26[b]	0.53	52					0.87[b]	1.50[b]	0.98	8

[a] Isomer shift: IS ± 0.03 mm/s; quadrupole splitting: QS ± 0.03 mm/s; line width: Γ ± 0.05 mm/s; spectral contribution: A ± 5%. Co$_9$S$_8$: IS = 0.26 mm/s; QS = 0.26 mm/s.[5] CoS$_{1+x}$: IS = 0.42 mm/s; QS = 0.61 mm/s.[5] [b] Fixed during fit.

the growth and/or increase in ordering of highly dispersed Co−sulfide particles to particles which finally will show in MES the IS and QS values of Co$_9$S$_8$.

From a similar MES and EXAFS study on the sulfidation of CoNaY(ion ex),[1] we have concluded that this picture also holds for ion-exchange type NaY-supported Co−sulfide species. In the following, the formation of Co−sulfide particles during a stepwise sulfidation of Co/NaY(imp) and Co/CaY(imp) prepared by pore volume impregnation will be discussed.

Wet Co/NaY(imp) and Co/CaY(imp). It is known that for calcined wet Co/NaY(imp) and Co/CaY(imp) Co−oxide species are present at the internal and/or external zeolite surface, whereas for CoNaY(ion ex) Co^{2+} ions surrounded by H$_2$O are present in the supercages of the zeolite.[26] However, the spectra of the wet fresh (non sulfided) Co/NaY(imp), Co/CaY(imp) and

CoNaY(ion ex)[1] are rather similar. It turned out that the spectra have no resemblance with those observed for bulk CoO[7] and Co$_3$O$_4$.[7,27] They are quite similar to those observed for fresh (non-sulfided) Co/C and CoMo/C[8,13] as well as Co/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$.[10,13] However, in these cases we are not able to assign the different spectral components of the fresh zeolite Y-supported Co samples to known bulk Co compounds.

Table 4 shows the similarity of the QS values for wet fresh (non-sulfided) Co/NaY(imp), Co/CaY(imp), and CoNaY(ion ex). However, in Table 4 it is also shown that upon room-temperature sulfidation the QS value is decreased and the spectral contribution is increased for the impregnated samples, whereas the ion-exchanged sample shows hardly any change. It is interesting to note that this difference in sulfidation behavior at room temperature is the only indication that different Co

TABLE 4: MES Parameters of the Co−Sulfide Doublet for Wet and Dry Co/NaY(imp), Co/CaY(imp), and CoNaY(ion ex), Fresh and Sulfided at 300 K

T_{sulf} (K)	QS (mm/s)	A (%)	QS (mm/s)	A (%)	QS (mm/s)	A (%)
	wet Co(4.0)/NaY(imp)		wet Co(3.8)/CaY(imp)		wet Co(3.2)NaY(ion ex)	
fresh	0.91	50	1.02	44	0.99	50
300 K	0.79	71	0.71	90	1.03	59
	dry Co(4.5)/NaY(imp)		dry Co(4.6)/CaY(imp)		dry Co(4.5)NaY(ion ex)	
fresh	0.94	55	1.16	64	1.05	48
300 K	1.41	53	1.23	64	1.35	56

species are present in the wet impregnated type and ion-exchange type starting materials.

For low sulfidation temperatures ($\leq$373 K) a high-spin 2+ contribution is found in the spectra of all wet catalysts, indicating the presence of a Co−O interaction. During sulfidation at 473 K this high-spin 2+ contribution has disappeared completely. As observed for wet CoNaY(ion ex),[1] also for wet Co/NaY-(imp) and Co/CaY(imp) a spectral contribution with an IS value around 0.38 mm/s and a QS value around 0.70 mm/s is found. Its spectral contribution has decreased after sulfidation at 573 K and has disappeared after the final sulfidation step at 673 K. The parameters of this spectral component correspond with those of CoS_{1+x} ($0.06 \leq x \leq 0.18$)[5] (see legend of Table 1) having the NiAs structure with cobalt atoms octahedrally surrounded by sulfur.[18] The formation of CoS_{1+x} is accompanied by a sudden decrease of the QS value of the highly dispersed Co−sulfide species (IS = 0.25 mm/s) to a value observed for bulk Co_9S_8. Both effects seem to be due to the presence of the physisorbed water in the zeolite as these effects are not observed whenever the physisorbed water is removed prior to sulfidation.

In Figure 2 the "averaged" QS values of the Co−sulfide species (IS = 0.19−0.27 mm/s) formed in the wet Co/NaY-(imp), Co/CaY(imp), and CoNaY(ion ex)[1] are presented as a function of the sulfidation temperature. It follows that in all three wet samples a Co_9S_8-like species (QS $\approx$ 0.22 mm/s) is already formed during sulfidation at 473 K. As shown in Tables 1 and 3 and in ref 1 for CoNaY(ion ex), the amount of this Co_9S_8-like species increases with increasing sulfidation temperature at the expense of the CoS_{1+x} phase. This CoS_{1+x} is an intermediate phase in the transition from highly dispersed Co−sulfide entities to Co_9S_8 species. The Co−K edge EXAFS measurements of stepwise sulfided wet CoNaY(ion ex)[1] showed an appearance and increase of contributions at longer distances in the radial distribution function after sulfidation at higher temperatures (473−673 K). Hence, it is rather likely that sulfidation of wet Co/NaY(imp) and Co/CaY(imp) also leads to the formation of Co−sulfide species with increasing particle size and/or ordering.

The formation of such rather large Co−sulfide species is confirmed by earlier HREM studies.[28,29] These studies showed the presence of Co−sulfide particles on the outer surface of wet sulfided Co/CaY(imp,673 K) with a size as large as 50 nm, although also some particles were found with a size of 3 nm. In addition, the determined overall metal:sulfur ratio of 9:8.2 of a wet Co/CaY(imp,673 K) sample indicated that the system was sulfided to Co_9S_8,[28,29] the metal sulfide phase which is to be expected on the basis of thermodynamics.[30] Also for sulfided zeolite-supported Ni catalysts similar results are obtained by Welters et al.[15,28]

Summarizing, it can be concluded that sulfidation of Co on wet Y-type zeolites at temperatures $\geq$473 K leads to a Co−sulfide phase with MES parameters of bulk Co_9S_8. Furthermore, by extrapolating the EXAFS results of de Bont et al.[1] for CoNaY(ion ex) and the HREM and overall metal:sulfur ratio results of Welters[28,29] it is rather likely that large Co_9S_8 particles
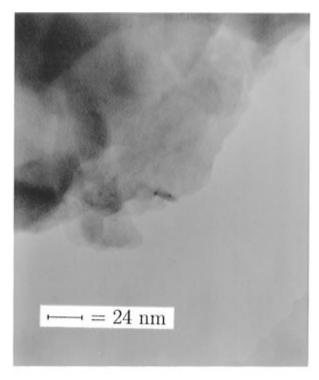
are formed on the outer surface of the Y-zeolite. The formation of these Co_9S_8 particles takes place via the intermediate CoS_{1+x} phase.

Dry Co/NaY(imp) and Co/CaY(imp). In general, it is observed that the normalized resonant absorption area (RAA) of the spectra increases upon the drying treatment in He. This increase of RAA indicates that the Co atoms become more fixed (or bonded) in the zeolite system.

Remarkable differences in sulfidation behavior of dry and wet Co/NaY(imp) and Co/CaY(imp) are observed. First, it turns out that already the 300 K sulfidation is influenced by the presence or absence of physisorbed water in the zeolite. The QS value of the Co−sulfide doublet of dry Co/NaY(imp,300 K) and Co/CaY(imp,300 K) is larger than that of the doublet of the fresh samples (see Table 4), in contrast to the results for wet Co/NaY(imp) and Co/CaY(imp). Second, in the case of dry Co/NaY(imp) and Co/CaY(imp) the high-spin 2+ contribution (Co−O interaction) is still present after sulfidation at 473 K (see Table 1), while it has disappeared at this temperature for their wet counterparts. Third, the formation of CoS_{1+x} as an intermediate state in the transition from highly dispersed Co−sulfide entities to Co_9S_8 species (with a QS $\approx$ 0.22 mm/s) has not been observed for the dry catalysts. Finally, the averaged QS value (see Figure 2) of the Co−sulfide species with IS between 0.19 and 0.27 mm/s formed in dry Co/NaY(imp) and Co/CaY(imp) decreases gradually to a value reported for Co_9S_8,[5] whereas for their wet counterparts the QS value (IS = 0.19−0.27 mm/s) decreases much more rapidly. In the dry CoNaY-(ion ex) catalyst the QS value of the Co−sulfide species formed remains much higher after sulfidation at 673 K (QS = 0.63 mm/s), indicating highly dispersed Co−sulfide species (see Figure 2).

The EXAFS results of dry Co/NaY(imp,473 K) show the presence of Co−O and Co−S contributions pointing to incomplete sulfidation of the Co particles at 473 K. Furthermore, no Co−Co contributions around 2.5 and 3.5 Å (typical for Co_9S_8 particles) are observed which indicates the presence of a well dispersed Co−sulfide phase. Most of the HREM pictures of this dry sample (such as the one presented in Figure 6a) shows only a few Co−sulfide particles at the outer zeolite surface (about 20 nm). Using a higher resolution, mainly only the zeolite lattice is observed while EDX shows that also Co and S are present. This is in line with the negligible amount (2%) of Co_9S_8 phase found in the MES spectrum after the more detailed analysis (with two different cobalt−sulfide phases: one with a QS = 0.26 and one with a QS $\approx$ 0.80 mm/s). The part (80%) of the cobalt−sulfide phase present as highly dispersed Co−sulfide species (QS $\approx$ 0.80 mm/s) confirms the results found in the EXAFS study. However, the amount of highly dispersed Co−sulfide species decreases upon increasing sulfidation temperature in favor of the Co_9S_8 particles.

In nearly all HREM pictures of Co/NaY(imp,673 K) large cobalt−sulfide particles are observed at the outer zeolite surface (such as the one presented in Figure 6b), confirming the results found in the EXAFS study. The same observation (HREM) holds for dry Co/CaY(imp,673 K) however the amount of large cobalt−sulfide particles at the outer surface of the zeolite is
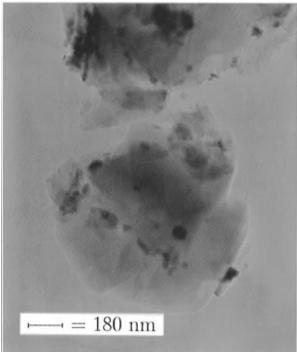
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Figure 6. HREM pictures of (a, top) dry Co/NaY(imp, 473K) and (b, bottom) dry Co/NaY(imp, 673 K).

less than for dry Co/NaY(imp,673 K). These observations confirm the MES results (Tables 1 and 3) showing that also the amount of Co_9S_8 present in Co/CaY(imp,673 K) is smaller than in Co/NaY(imp,673 K). For CoNaY(ion ex) however, no Co—sulfide particles are found at the outer surface of the zeolite with HREM after sulfidation at 673 K, indicating that in this case the highly dispersed Co—sulfide particles are located inside the NaY supercages.

From Tables 1 and 3 it is clear that in the MES spectra of dry Co/NaY(imp,673 K) and Co/CaY(imp,673 K) besides a contribution characteristic for well-ordered Co_9S_8 also a significant contribution (24% and 40%, respectively) characteristic for highly dispersed Co—sulfide (QS value of about 0.79 mm/s) is still present. Most probably, this highly dispersed Co—
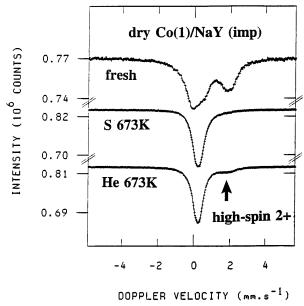

Figure 7. MES spectra of dry Co(1)/NaY(imp) (fresh, sulfided at 673 K and He-treated at 673 K).

sulfide is also located inside the supercages such as in case of CoNaY(ion ex,673 K) and its potential precursors are Co—chloride, Co—oxide, and Co^{2+} cations introduced in these supercages via impregnation, wet ion exchange (during the wet stage of the impregnation procedure), and solid-state ion exchange[31] (during calcination and/or drying in He at 673 K). From the comparison of the temperature dependency of the Co—sulfide contribution in the 473, 573, and 673 K MES spectra of dry Co/NaY(imp) and dry Co/CaY(imp) on one hand and dry CoNaY(ion ex)[1] on the other, one might conclude that the Co—sulfide species still present in Co/NaY(imp) and Co/CaY(imp) after sulfidation at 673 K (25% and 40%, respectively) originate from (solid state) ion exchanged Co^{2+} cations. According to this line of reasoning, the part of the formed Co—sulfide species that disappeared during sulfidation at 573 and 673 K originates from Co—chloride or Co—oxide deposited in the supercages via impregnation and migrates when the sulfidation temperature is increased (from 473, 573, to 673 K) to the outer NaY surface to form Co_9S_8 particles.

The presence of highly dispersed Co—sulfide entities is also found for a 1 wt % Co/NaY(imp). After the dry sulfidation procedure up to 673 K (see Figure 7) the presence of Co_9S_8 particles (75%) together with highly dispersed Co—sulfide entities (18%) and a small high-spin 2+ contribution (7%) is observed in the MES spectrum. After sulfidation, the dry Co-(1)/NaY(imp) has been treated in He at 673 K for 5 h. The resulting MES spectrum (see Figure 7) clearly shows an increase of the high-spin 2+ contribution. Its spectral contribution has become 19%. As shown by de Bont et al.[32] and Vissenberg et al.,[33] it is possible to decompose highly dispersed Co—sulfide particles located in the supercages of CoNaY(ion ex) upon a He treatment at 673 K. This decomposition is explained by the protolysis reaction: $CoS_x + 2H^+ \rightarrow H_2S + Co^{2+}$ (in NaY cation positions). It is reasonable to assume that the increased high-spin 2+ contribution observed in the MES spectrum of the He-treated Co(1)/NaY(imp,673 K) is also caused by a protolysis reaction between highly dispersed Co—sulfide and protons both present inside the supercages. So, the MES results shown in Figure 7 support the above statement that not only dry sulfided CoNaY(ion ex) but also dry sulfided Co/NaY(imp) and Co/CaY(imp) contain highly dispersed Co—sulfide species inside the supercages.

It can be concluded from Figure 2 and Tables 1 and 3 that the growth of the Co−sulfide species in the Co/CaY(imp) and Co/NaY(imp) catalysts can be retarded by removal of the physisorbed water prior to sulfidation. This retardation is more pronounced for Co/CaY(imp) than for Co/NaY(imp). Although drying of the impregnated samples prior to sulfidation helps to reduce the formation of Co_9S_8 particles at the outer zeolite surface, drying turns out to be much less effective than in the case of CoNaY(ion ex) samples. Especially for Co/NaY(imp) the drying effect is rather small. The discrepancy between the drying effect observed for Co/NaY(imp) and Co/CaY(imp) seems to be related with the presence of a larger Co fraction interacting relatively strongly with the zeolite Y lattice in the case of Co/CaY(imp). Whereas calcined and He-dried Co/NaY-(imp) was blue (indicating that the majority of the Co is present as anhydrous $CoCl_2$), its Co/CaY(imp) counterpart had a purple color very similar to the color of He-dried CoNaY(ion ex) in which Co is exclusively present as Co^{2+} cations rather strongly interacting with the zeolite Y lattice. The color similarity indicates that Co/CaY(imp) contains a considerable amount of Co^{2+} introduced via (solid state) ion-exchange (vide supra). This exchange process is possibly facilitated by the protons present in dry CaY.

The relatively strong Co−zeolite Y interaction in Co/CaY-(imp) is also reflected by lower sulfidation temperature dependency of the Co−sulfide and "high-spin 2+" spectral contributions in the 473−673 K range compared to Co/NaY(imp) (see *A* values in Tables 1 and 3). The same considerations can be applied to explain the differences between dry Co/CaY(imp) and dry CoNaY(ion ex).[1] In the latter catalyst Co is exclusively present as ion-exchanged Co^{2+} and preferentially located in the sodalite cages and hexagonal prisms, i.e., at the least accessible and most stable cation sites while in Co/CaY(imp) Co is only partly ion exchanged and the Co^{2+} cations are most likely located at less stable and better accessible sites in the supercages.[34,35]

The observed difference in highly dispersed Co−sulfide content between impregnation type Co/NaY(imp,673 K) and Co/CaY(imp,673 K) and ion-exchanged CoNaY(ion ex,673 K) might also be (partly) explained by assuming that the zeolite protons present after sulfidation (low electron density) have a stabilizing effect on the electron rich small Co−sulfide particles. Accordingly, the Co−sulfide content would increase with increasing proton acid strength: Co/NaY(imp) < Co/CaY(imp) < CoNaY(ion ex). However, Welters et al.[16] have not found support for this explanation in their study on sulfided Ni/H(x)-NaY(imp) catalysts varying in acidity.

As can be concluded from the results presented in this paper (Tables 1 and 3) and in ref,[1] all forementioned structural differences are irrelevant when Co/NaY(imp), Co/CaY(imp), and CoNaY(ion ex) are sulfided in the presence of physisorbed water (wet sulfidation).

Conclusions

Sulfidation of wet (hydrated) Co/NaY(imp) and Co/CaY(imp) results in the formation of large and/or better ordered Co_9S_8-like particles (Co_9S_8) on the outer surface of the Y-zeolite. The formation of these Co_9S_8 species takes place via the intermediate formation of CoS_{1+x} (with a NiAs structure).

Removal of the physisorbed water prior to sulfidation retards the formation of Co_9S_8 to such an extent that even after sulfidation at 673 K still a small amount of highly dispersed Co−sulfide entities are present and most likely located in the zeolite-Y supercages. Although for Co/CaY(imp) the effect of dry sulfidation is considerably stronger than for Co/NaY(imp), it stays well below the drying effect observed[1] for CoNaY(ion ex).

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