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Journal of Molecular Structure 410–411 (1997) 103–110

Journal of
MOLECULAR
STRUCTURE

Identification of SH groups in zeolite-supported HDS catalysts by FTIR spectroscopy

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Received 26 August 1996; accepted 19 September 1996

Abstract

NiNaY zeolite (prepared by ion exchange of NaY) and CoHY zeolite (prepared by impregnation of HY) were studied by Fourier Transform Infrared (FTIR) spectroscopy and by the thiophene hydrodesulfurization (HDS) catalytic reaction. The metal- (Ni or Co) loading in the nonsulfided zeolites correlated with the Lewis acidity (determined by pyridine adsorption) indicating a high dispersion level of Ni or Co species. Following sulfidation of the zeolites by H_2/H_2S at 373 K two kind of SH band were observed in the IR spectra: the broad band at 2520 cm^{-1} was assigned to H_2S hydrogen bonded to the strong Brönsted acid sites (SiOHAl groups), the sharp band at 2580 cm^{-1} was assigned to H_2S coordinatively bound to the Lewis acidic cationic sites. These SH bands were not identified during sulfidation above 473 K, but the similar catalytic activities and product selectivities after sulfidation either at 373 K or at 673 K indicate that SH groups bonded to strong Brönsted acid sites are present and should play a role in HDS catalysts working under industrial conditions. © 1997 Elsevier Science B.V.

Keywords: Catalysis; FTIR spectroscopy; HDS; SH groups; Zeolites

1. Introduction

SH groups can play an important role in the reaction mechanism of hydrodesulfurization (HDS). The Bond Energy Model (BEM) for HDS reactions [1] suggests that the sulfur vacancies or coordinatively unsaturated sites (CUS) of the metal sulfide active phase coordinate the heteroatom of the reactant and the neighboring SH groups might provide the hydrogen for the reaction. Direct evidence for the presence of SH groups in working HDS catalysts has not yet been found by infrared (IR) spectroscopy. The IR spectra of pyridine adsorbed at 673 K on sulfided (Co)Mo/Al_2O_3 catalysts showed the presence of weak Brönsted acid sites, which were attributed to SH species generated by dissociative H_2S reactions on the CUS sites [2], but the weak SH stretching vibration band around 2500–2600 cm^{-1} was not seen in the IR spectra, only a broad band around 3600 cm^{-1} was attributed to hydrogen-bonded OH-to-SH [3]. The presence of SH groups was not expected to be favored at Co (Ni) edge sites [3].

The adsorption of H_2S was studied on ZSM5 zeolites [4]. H_2S was found to be hydrogen-bonded to the SiOHAl groups of HZSM5 in two different positions—in linear (2580 cm^{-1}) and cyclic (2573 cm^{-1}) structures. H_2S adsorbed coordinatively

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PII S0022-2860(96)09484-7

on the Na^+ cation of NaZSM5 via the sulfur atom (2580 cm^{-1}) equivalent to the above mentioned linear structure. A broad band at 2566 cm^{-1} was assigned to H_2S adsorbed on extra lattice material.

2. Experimental

Nickel- and cobalt-containing faujasites were prepared by liquid-phase ion-exchange of NaY with aqueous $NiCl_2$ solutions (Ni2NaY, Ni4NaY and Ni6NaY) and by impregnation of NH_4Y with aqueous $Co(NO_3)_2$ solutions (Co2HY, Co4HY and Co6HY), where the number signifies the metal-loading (%, *w/w*) after calcination. The preparation methods are described in detail elsewhere [5,6].

The self-supporting wafers (~5 mg) of the above samples were activated in nitrogen (30 cm^3 min^{-1}) at 673 K for 1 h in an in situ IR flow cell. After cooling to 373 K in N_2, the zeolites were treated for 1 h in nitrogen (nonsulfided, NON) or in an 8% *v/v* H_2S-containing H_2 gas mixture (sulfided, SUL), respectively. Then the temperature was raised to 423 K (N_2 flush) and the samples were saturated with 4 μL pyridine injected into the nitrogen stream within 15 min. The type (Brönsted or Lewis) and concentration of their acidity was characterized by IR spectroscopy at 423 K followed by temperature-programmed desorption (TPD) of adsorbed pyridine up to 773 K. The IR spectra were recorded in a BOMEM FTIR spectrometer equipped with a DTGS detector (32 scans, 4 cm^{-1} resolution). The concentration of Brönsted and Lewis acid sites was calculated with the integral molar extinction coefficients of adsorbed pyridine IR absorption bands determined by Emeis [7].

The thiophene HDS test reactions were carried out at 673 K and atmospheric pressure in a flow reactor system using 30 cm^3 min^{-1} flow of 3% thiophene in H_2 following 1 h activation in N_2 at 673 K, nonsulfiding in nitrogen (NON) or sulfiding in H_2/H_2S at 373 K (SUL) or at 673 K (SULH). Thiophene and the products were detected using a GC equipped with a 3 m × $\frac{1}{8}$" i.d. *n*-octane/Porasil C column.

The catalytic activities are described by thiophene conversion (1 − unreacted thiophene/thiophene in feed), yield (products/(products + unreacted thiophene)) and C–S bond hydrogenolysis activity without C–C bond breaking (C_4 products/(products + unreacted thiophene)). We assigned the difference between conversion and yield to the quantity of thiophene remaining on the catalyst as coke. The difference between yield and C–S bond hydrogenolysis activity was used to calculate the amount of cracked products. Product selectivities were calculated from the composition of the product mixture: C_4 (C_4 products/all products), isomerization (isobutane/(isobutane + *n*-butane)) and hydrogenation ((isobutane + *n*-butane)/C_4 products) selectivities.

3. Results and discussion

The OH region (3800–3200 cm^{-1}) in the IR spectra of nonsulfided zeolites related to unit (1 mg) sample mass is shown in Fig. 1 before pyridine adsorption. The NaY sample has no band in this region, the NiNaY samples show two bands at 3633 and 3545 cm^{-1}, respectively, the (Co)HY zeolites exhibit three bands, the third line is at 3738 cm^{-1}. The band at 3738 cm^{-1} is attributed to nonacidic SiOH groups, the bands at 3633 and 3545 cm^{-1} are assigned partially to strong Brönsted acidic high frequency (HF) and low frequency (LF) SiOHAl bands, respectively [8]. Presumably $(NiOH)^+$ or $(CoOH)^+$ groups also contribute to the band of HF OH groups [9]. The presence of SiOH bands indicates some dealumination in the (Co)HY zeolites.

The pyridine IR absorption bands (1700–1400 cm^{-1}) of nonsulfided zeolites saturated with pyridine at 423 K are shown in Fig. 2. The band at 1541 cm^{-1} is assigned to pyridinium ions adsorbed on Brönsted acid sites [10]. The intensity of this band is very low in the (Ni)NaY zeolite and decreases with metal-loading in the CoHY samples in parallel with the OH bands in Fig. 1. The bands at 1442–1454 cm^{-1} are attributed to pyridine coordinatively adsorbed on Lewis acid sites [10]. The IR spectrum of NaY zeolite contains a singlet Lewis acidic band at 1442 cm^{-1} but a new Lewis acid band appears at 1454 cm^{-1} in the NiNaY samples and the intensity of the latter band increases with the nickel content. The spectra of (Co)HY zeolites show two bands at 1442 and 1448 cm^{-1}, respectively. The doublet band at 1442–1454 cm^{-1} indicates that at least two kinds of Lewis acid site are present in all samples except NaY.

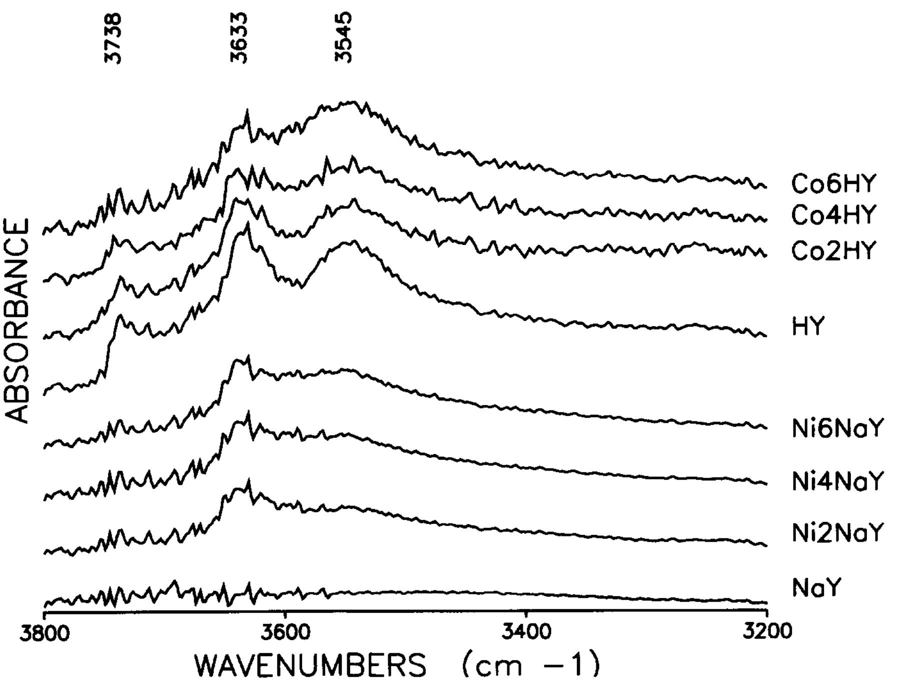

Fig. 1. OH bands in the IR spectra of nonsulfided zeolites at 423 K. (Bands of (Ni)NaY are multiplied by 1.75.)

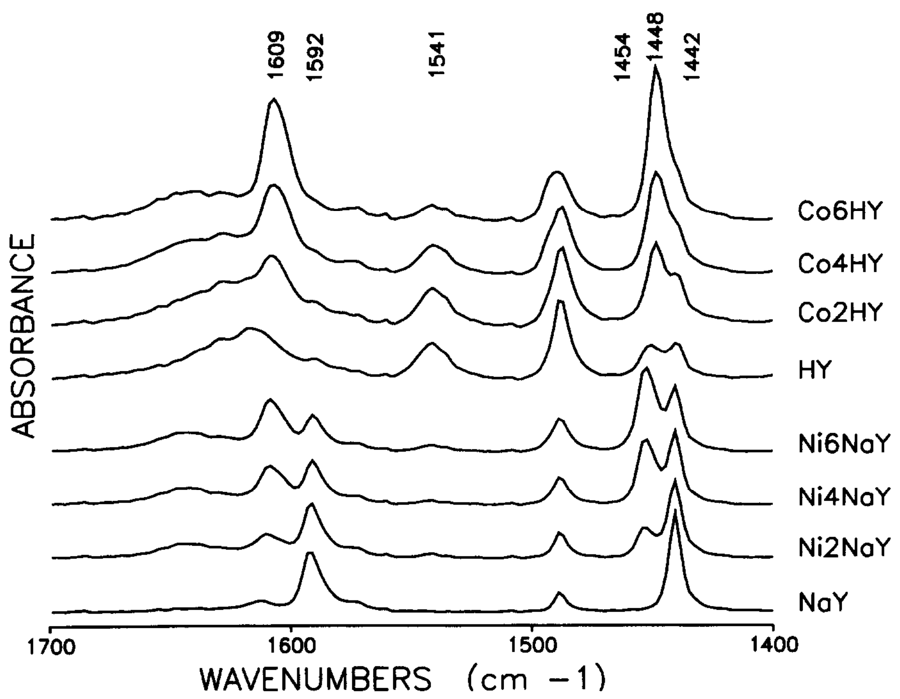

Fig. 2. Pyridine IR absorption bands of nonsulfided zeolites after saturation with pyridine at 423 K.

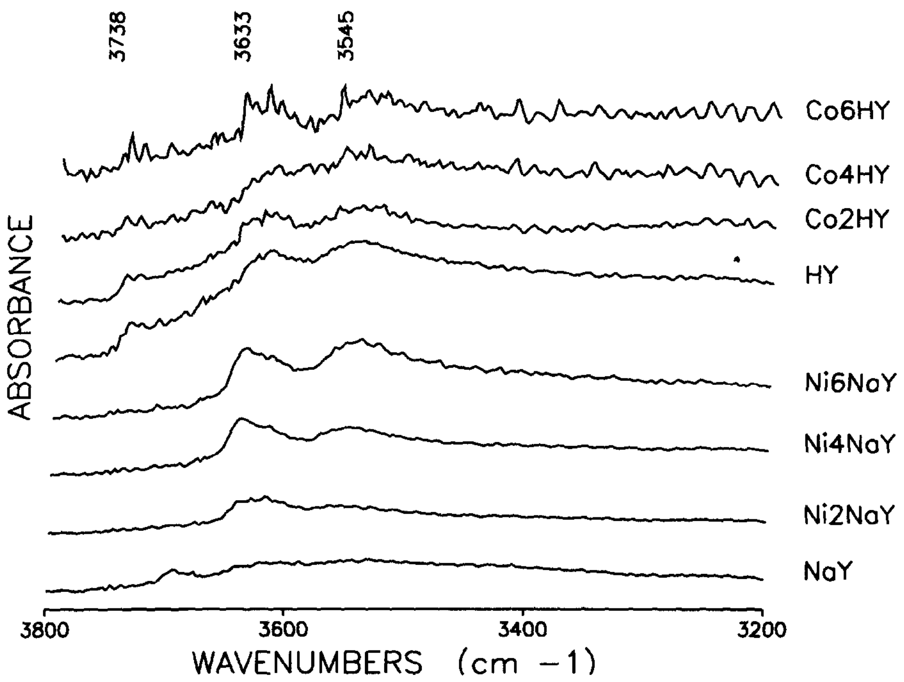

Fig. 3. OH bands in the IR spectra of sulfided zeolites at 423 K before pyridine absorption.

The band at 1609 cm^{-1} (NiNaY, CoHY) is assigned to pyridine coordinatively bonded to nickel or cobalt cations [11]; its intensity increases with the Ni or Co content (Fig. 2). Corma et al. [11] observed a band at 1598 cm^{-1} related to pyridine coordinated to Na$^+$ ions, the position of this band is 1592 cm^{-1} in our (Ni)NaY spectra and its intensity decreases with increasing nickel content. The intensity of Lewis acidic bands at 1609 and 1454 or 1448 cm^{-1} increases in parallel with the nickel- or cobalt-loading, respectively, therefore these bands are assigned—at least partially—to pyridine bound to nickel or cobalt species.

The OH region in the IR spectra of sulfided zeolites before pyridine adsorption is shown in Fig. 3. The intensity of HF and LF SiOHAl bands increases with the nickel-loading in the spectra of NiNaY samples, but it seems to decrease with cobalt content in the case of CoHY zeolites. Comparing the OH region before (Fig. 1) and after (Fig. 3) sulfidation, the band intensities are higher in sulfided (Ni)NaY but lower in sulfided (Co)HY zeolites.

The SH region (2700–2400 cm^{-1}) in the IR spectra of sulfided zeolites before pyridine adsorption is shown at 373 K in Fig. 4. Sharp (2580 cm^{-1}) and broad (2520 cm^{-1}) SH stretching bands are observed on all zeolites except NaY (only sharp band). The sharp band is assigned to H_2S coordinatively adsorbed on Lewis acidic cationic sites, mainly on Na$^+$ ions, in accordance with [4]. We assign the broad band to H_2S hydrogen-bonded to the strong Brönsted acid sites (SiOHAl groups) contrary to [4], because we saw previously (Fig. 1) and we shall see later (Table 1) that the NiNaY zeolites do not contain extralattice alumina.

The pyridine IR absorption bands of sulfided zeolites saturated with pyridine at 423 K are shown in Fig. 5. The position of Brönsted and Lewis acidic bands hardly changes during sulfidation (compare with Fig. 2), but the bands at 1454 and 1612 cm^{-1}, which were assigned to pyridine coordinatively bonded to nickel or cobalt cations in Fig. 2, almost completely disappear. The intensity of Brönsted related to Lewis acidic bands is much higher in the sulfided (Fig. 5) than in the nonsulfided (Fig. 2) faujasites (see also Table 1).

The pyridine IR absorption bands of sulfided faujasites during TPD of pyridine at 573 K are shown in Fig. 6. The bands at 1440 and 1592 cm^{-1} are hardly

Table 1

Brönsted (*B*) and Lewis (*L*) acidity (mol kg^{-1}) and *B*/*L* concentration ratios of nonsulfided (NON) and sulfided (SUL) zeolites after saturation with pyridine at 423 K and separation of Lewis acidic band of pyridine (1442–1454 cm^{-1}) into weak (weak), extralattice Al (exAl) and nickel/cobalt (Ni/Co) ion sites

Sample	Concentration (mol kg^{-1})			Separation of Lewis band		
	B	*L*	*B*/*L*	Weak	exAl	Ni/Co
NaY NON	0.03	1.62	0.02	1.62	0	0
Ni2NaY NON	0.11	1.92	0.06	1.47	0	0.45
Ni4NaY NON	0.17	2.48	0.07	1.32	0	1.16
Ni6NaY NON	0.26	2.79	0.09	1.22	0	1.57
NaY SUL	0.21	0.69	0.30	0.69	0	0
Ni2NaY SUL	0.38	0.57	0.66	0.57	0	0
Ni4NaY SUL	0.83	0.45	1.82	0.43	0	0.02
Ni6NaY SUL	1.12	0.34	3.49	0.25	0	0.09
HY NON	1.54	1.35	1.14	0.72	0.63	0
Co2HY NON	1.61	2.33	0.69	0.88	0.63	0.82
Co4HY NON	1.24	2.88	0.43	1.00	0.63	1.25
Co6HY NON	0.67	3.66	0.18	1.05	0.63	1.98
HY SUL	0.96	0.54	1.77	0.23	0.31	0
Co2HY SUL	1.39	0.73	1.90	0.25	0.31	0.17
Co4HY SUL	1.61	0.74	2.18	0.26	0.31	0.17
Co6HY SUL	1.69	0.75	2.25	0.28	0.31	0.16

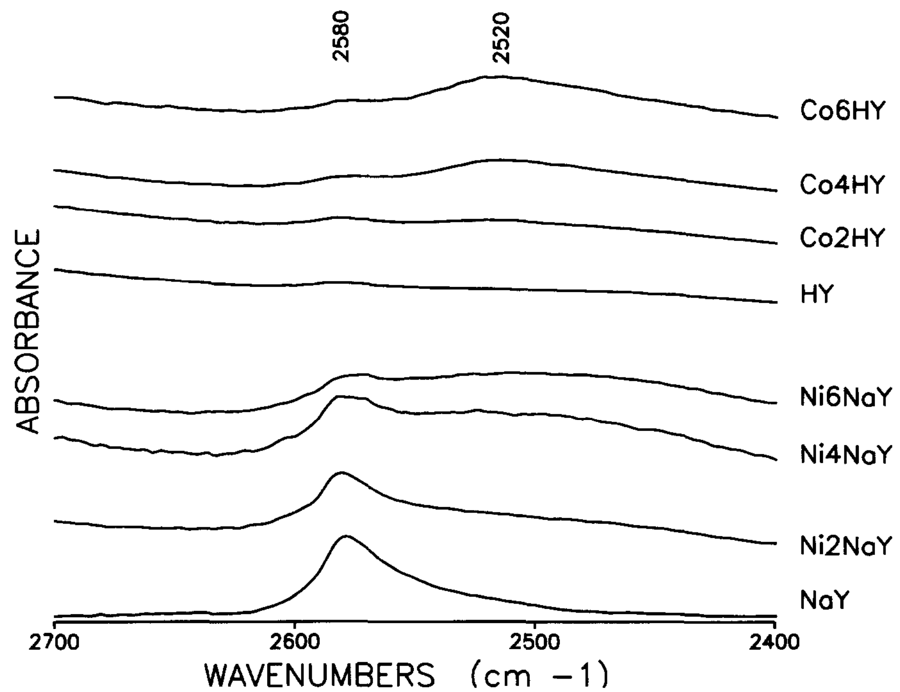

Fig. 4. SH bands in the IR spectra of sulfided zeolites at 373 K. (Bands of (Ni)NaY are multiplied by 8.)

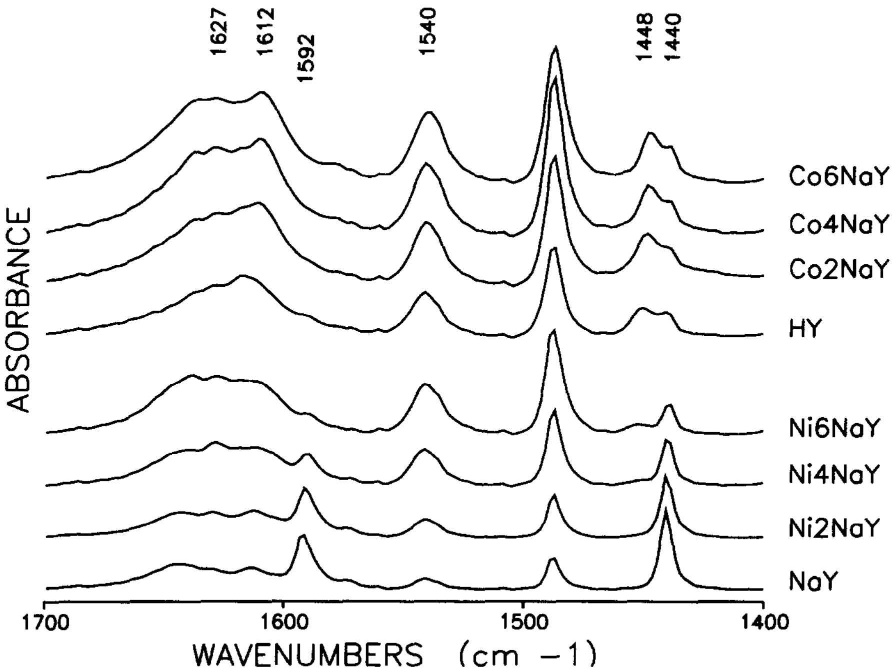

Fig. 5. Pyridine IR absorption bands of sulfided zeolites after saturation with pyridine at 423 K.

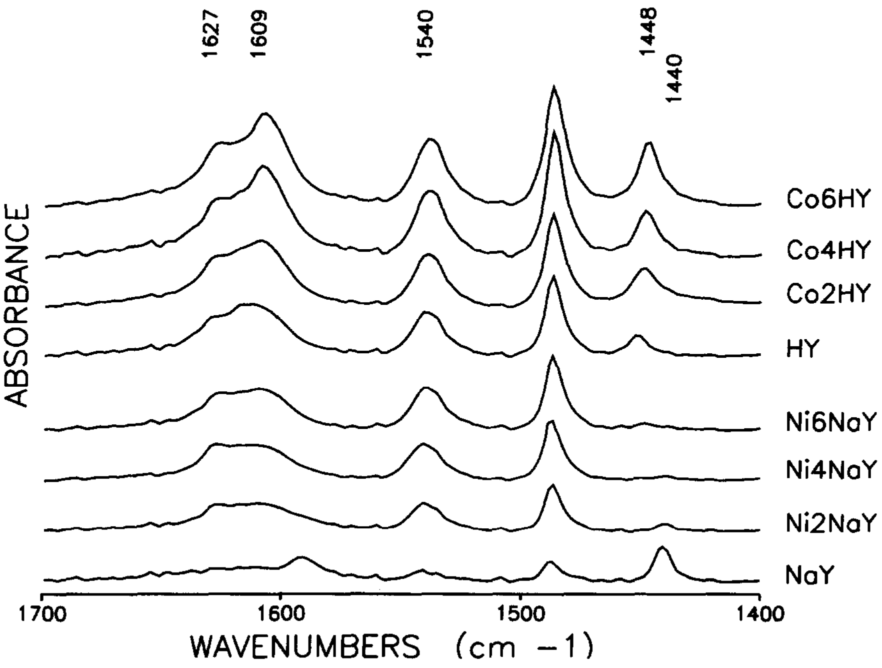

Fig. 6. Pyridine IR absorption bands of sulfided zeolites during TPD of pyridine at 573 K.

seen in the spectra (except NaY) at this temperature; they are, therefore, attributed to weak Lewis acidic species. The Lewis acidic bands of NiNaY almost disappear at 573 K. The band at 1448 cm^{-1} is attributed partially to extralattice Al^{3+} (HY and CoY) and partially to Co^{2+} (CoY) Lewis acidic sites, respectively.

The concentration of acid sites calculated from the intensity of pyridine absorption bands at 1541 cm^{-1} (Brönsted) and 1442–1454 cm^{-1} (Lewis) is shown in Table 1. The concentration of Brönsted acid sites increases slightly with nickel-loading (NiNaY) but decreases with the cobalt-loading (CoHY) before sulfidation, in accordance with the OH spectra (Fig. 1). The increase of Brönsted acidity with nickel-loading (NiNaY) is much higher after sulfidation, again in accordance with the OH spectra (Fig. 3), but it seems not true for the CoHY zeolites: the OH band intensities of CoHY decrease after sulfidation (compare Fig. 3 with Fig. 1), but the Brönsted acidities of Co4HY and Co6HY increase (Table 1). The intensive 'broad' SH bands (2520 cm^{-1}) of these zeolites (Fig. 4) exhibit H_2S adsorbed on the strong Brönsted acidic SiOHAl groups causing low OH-band intensities in Fig. 3, but this acidity partially recovers after pyridine adsorption. Competitive adsorption was observed between H_2S and pyridine for the acid sites of HY [6] and between thiophene and pyridine in HDS catalysts [12]. The intense 'sharp' SH bands (2580 cm^{-1}) of (Ni)NaY zeolites (Fig. 4) explain the high decrease of Lewis acidity of these samples after sulfidation (Table 1) by some adsorption of H_2S on the Lewis acidic Na^+ sites. This adsorption also creates new Brönsted acidity (NaY: from 0.03 to 0.21 mol kg^{-1}).

Two or three types of Lewis acid site are observed on the NiNaY or CoHY samples, respectively; the band at 1442–1454 cm^{-1} is separated into two or three contributions assigned to weakly acidic Lewis acid sites (1442 cm^{-1}), extralattice Al (1448 cm^{-1} only in (Co)HY)), and Ni (1454 cm^{-1}) or Co (1448 cm^{-1}) species (Table 1). For estimating the number of Co sites a constant concentration of extralattice Al species is assumed: 0.63 (NON) or 0.31 (SUL). The concentration of Lewis acidic nickel or cobalt species increases with the metal-loading in the nonsulfided catalysts (Table 1). After sulfidation the quantity of Lewis acidic nickel or cobalt ions decreased significantly; we conclude, therefore, that nickel and cobalt are sulfided to a high extent in these zeolites. We attribute the decrease of weak and extralattice Al Lewis acidity during sulfidation to the possible adsorption of H_2S on these species.

We saw that the presence of SH bands resulted in an increase of Brönsted acidity and a decrease of Lewis

Table 2

Thiophene conversions (Conv.), C–S bond hydrogenolysis activities (C–S ac.), cracking (Crack.), coking, C_4 (C_4 sel.), isomerization (Iso. sel.) and hydrogenation (Hyd. sel.) selectivities (/%) of variously pretreated (NON, SUL, sulfided at 673 K = SULH) zeolite catalysts

Catalyst	Pretreat.	Conv.	C–S ac.	Crack.	Coking	C_4 sel.	Iso. sel.	Hyd. sel.
Ni2NaY	NON	8.2	1.7	0.8	5.7	70	77	3.5
	SUL	36	20	2.7	14	88	66	9.0
	SULH	35	16	2.3	17	88	66	6.0
Ni4NaY	NON	20	4.7	2.4	13	66	85	19
	SUL	53	30	6.5	17	82	78	26
	SULH	53	30	5.6	18	84	77	18
Ni6NaY	NON	27	6.1	3.1	17	66	87	27
	SUL	77	53	10	14	84	77	33
	SULH	63	38	8.1	16	83	79	26
Co2HY	NON	27	0.3	0.8	26	25	91	39
	SUL	22	0.1	0.2	21	30	91	38
	SULH	22	1.9	2.1	18	47	90	31
Co4HY	NON	32	1.0	1.5	29	39	90	37
	SUL	33	2.4	2.7	28	47	90	40
	SULH	60	19	12	28	62	85	42
Co6HY	NON	42	4.4	4.6	33	49	89	39
	SUL	89	47	21	21	69	83	59
	SULH	75	30	16	28	65	82	46

acidity during sulfidation at 373 K. The industrial HDS reactions proceed at temperatures higher than 373 K. The sharp SH band disappears but the broad one survives during heating from 373 K to 473 K in nitrogen or sulfidation at 473 K showing the weaker adsorption of H_2S on the Lewis than on the Brönsted acid sites. SH bands cannot be identified during sulfidation at 573 K or higher temperature, but we studied the thiophene HDS activities and product selectivities following sulfidations at 373 K and 673 K in order to clarify the presence or possible role of SH groups in this reaction.

Thiophene conversions, within these three different activities and three kinds of selectivity measured after NON, SUL or SULH pretreatments over the zeolite catalysts are shown in Table 2. Most activities (mainly the most important C–S hydrogenolysis activity to the detriment of coking) and selectivities (except isomerization) increase with metal-loading and sulfidation temperature. The isomerization and hydrogenation selectivities of more Brönsted acidic CoHY zeolites were always higher than those of appropriate NiNaY samples. Generally the catalytic characteristics of SUL samples are closer to the SULH than to the nonpretreated zeolites. Therefore we suppose that SH groups bonded to strong Brönsted acid sites should be present and should play a role in HDS catalysts working under industrial conditions.

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