Hydrogen–Deuterium Equilibration over Transition Metal Sulfide Catalysts: On the Synergetic Effect in CoMo Catalysts

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H_2–D_2 equilibration was used to study the synergetic effect between Co and Mo in carbon-supported CoMo sulfide catalysts. The reaction was carried out in a recirculation apparatus with continuous on-line analysis of all gas-phase components (H_2, D_2, HD, H_2S, D_2S, and HDS) by a mass spectrometer. The low reaction temperature (423 K) allowed for the first time a comparison to be made of the catalytic activity between Co sulfide particles in low-temperature sulfided (373 K) carbon-supported Co and those in standard sulfided (673 K) carbon-supported CoMo, which have similar ^{57}Co MES parameters. On the basis of the much higher activity of the bimetallic catalyst than of the monometallic catalysts (Co and Mo sulfide) it is concluded that the observed synergy is related neither to the effect of the high dispersion of the Co sulfide nor seemingly to spillover effects as put forward by the remote control model. The results indicate that the sulfur atoms that bridge between Co^{2+} and Mo^{4+} play a crucial role during the catalytic cycle. During the equilibration reaction also extensive exchange takes place between hydrogen (deuterium) atoms adsorbed on the sulfided phase and hydrogen atoms present at the carbon support surface. This spillover process is accelerated by admixture of H_2S, which most probably leads to an increase of terminal SH groups by dissociative H_2S adsorption. These SH groups are thought to form hydrogen bridges with the carbon support functional groups. Both H_2 and H_2S compete for adsorption on the same coordinatively unsaturated sites. While heterolytic dissociation of H_2 is considered to lead to a hydride and a bridging SH group between Co and Mo, heterolytic dissociation of H_2S would lead to the formation of two SH groups, one bridging SH group and one terminal SH group active in forming hydrogen bridges with the support surface functional groups. © 1999 Academic Press

Key Words: hydrotreatment; sulfide catalysts; Co–Mo–S; synergy; active site; promoter effect; thiophene HDS; H_2–D_2 equilibration; hydrogen; deuterium.

INTRODUCTION

Whereas the use of Co(Ni)Mo sulfide catalysts to desulfurize oil fractions has been well established and has gone on now for close to a century, the molecular basis of the synergetic effect between Co and Mo is still a subject of intense debate. It is generally accepted that in the active phase, small cobalt sulfide species are located at the MoS_2 edges (1). From combined Mössbauer emission spectroscopy (MES) and thiophene hydrodesulfurization (HDS) activity measurements (2, 3) it was proposed that Co is present in a unique phase, designated the "Co–Mo–S" phase. More detailed MES measurements showed that a unique Co–Mo–S phase as such does not exist: the Co sulfide species located at the MoS_2 edges may differ locally in size and ordening (4), a fact that was confirmed by EXAFS measurements (5).

Vissers *et al.* (6) concluded that the intrinsic HDS activity of carbon-supported Co (Co/C) sulfided at 673 K approaches the activity of CoMo/C. From MES studies (7, 8) it was established that the local environment of Co in Co/C sulfided at 373 K is equal to that of Co in sulfided CoMo/C. Furthermore, it appeared that during sulfidation at higher temperatures the very small cobalt sulfide species initially present in Co/C sinter, resulting in a Co_9S_8-type phase after sulfidation at 673 K. Later, EXAFS measurements (9) showed that the local environment of Co in Co/C sulfided at 373 K and in CoMo/C sulfided at 673 K are very similar. These findings were taken as a strong indication that the high activity of CoMo/C is related to a highly dispersed Co sulfide species stabilized at the edge surface of MoS_2 rather than to a mixed CoMo sulfide species. The remote control model by Delmon (10–12) and the vacancy model by Nørskov and co-workers (13, 14) are alternative explanations for the high activity of CoMo-based catalysts. The remote control model describes the synergetic effect in these catalysts in terms of spillover hydrogen being produced on Co_9S_8 particles and creating vacancies on the active component, i.e., MoS_2. According to the vacancy model the sulfur bond energy is decreased in Co–Mo–S compared to MoS_2 thus leading to an increase in the number of vacancies. It is this parameter that controls the activity of transition metal sulfides (TMS). Indeed, recent first principle calculations (14) find a weakening of the Mo–S–Co bonds and easy creation of surface vacancies.

To test the hypothesis that Co sulfide is the active component in hydrotreating catalysts and that MoS_2 acts only as a secondary support to hinder CoS_x sintering, catalytic activity measurements are necessary. The most frequently

applied test reactions (e.g., thiophene HDS) are carried out at high temperatures (typically 523 K or higher) in order to activate carbon–heteroatom bonds. At these high temperatures Co sulfide species obtained after low-temperature sulfidation are not stable and transform into Co_9S_8-type species.

Since activation of hydrogen over MoS_2 catalysts occurs readily at ambient temperature at the edge surface (15, 16), the equilibration reaction between hydrogen and deuterium was used to clarify this issue. Based on the above-mentioned studies (7–9) Co/C and (Co)Mo/C catalysts were selected. CoNaY was also included in this study, because it was shown that inside zeolite micropores highly dispersed cobalt sulfide particles can be formed (17–19).

The aim of the present study is to determine the role of Co and Mo in sulfided CoMo catalysts, i.e., MoS_2 being a secondary support for active CoS_x clusters or being constitutive in the active phase itself.

METHODS

Catalyst Preparation

Carbon-supported Mo-containing catalysts (Mo/C; CoMo/C) were prepared by pore volume impregnation with ammoniacal solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck, >99.9%) and $Co(NO_3)_2 \cdot 6H_2O$ (Merck, p.a.). In the case of CoMo/C nitrilotriacetic acid (NTA) was used as a complexing agent according to the procedure described by Van Veen *et al.* (20). A suite of six Co-containing catalysts (Co/C) was prepared by pore volume impregnation with aqueous $Co(NO_3)_2 \cdot 6H_2O$ solutions of appropriate concentration. A 125- to 250-μm sieve fraction of an activated carbon (NORIT RX3-extra) having a surface area of 1197 m^2/g and a pore volume of 1.0 ml/g was used as carrier material. After impregnation, the catalysts were dried in static air at room temperature for 1 h and subsequently at 383 K for 12 h. Ion-exchanged CoNaY (3.9 wt% Co) was obtained by exchanging NaY (Akzo, $Na_{55}(AlO_2)_{55}(SiO_2)_{137}$, containing 25 wt% physisorbed water) with a solution of $CoCl_2$ of appropriate concentration followed by washing until Cl^- free and drying in air at 383 K for 16 h.

The metal contents of the different catalysts were determined by atomic absorption spectroscopy and are listed in Table 1. Co/C containing 5.9 wt% Co was taken as the standard carbon-supported Co catalyst. Prior to reaction, the carbon-supported samples were sulfided *in situ* in a flow (60 Nml/min) of 10% H_2S in H_2 (Hoekloos, >99.5%). The catalysts were heated to the final sulfidation temperature at a heating rate of 6 K/min (in the case of CoMo/C: 2 K/min). The sample was then kept at this temperature for 2 h.

Prior to sulfidation, CoNaY was dehydrated by heating the catalyst in flowing argon (flow rate: 60 Nml/min) at a rate

TABLE 1

Metal Contents of the Prepared Catalysts

Catalyst	Metal salt	Metal loading (wt%)
MoS_2	Powder (Janssen Chimica, 99+%)	
Mo/C	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck)	7.6
Co/C	$Co(NO_3)_2 \cdot 6H_2O$ (Merck)	0.04; 0.25; 0.44; 0.96; 3.2; 5.9; 7.0
CoMo/C	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	6.0
	$Co(NO_3)_2 \cdot 6H_2O$	1.3
	$N(C_3H_7O)_3$ (ACROS, >97%)	1.2 mol NTA/mol Mo
CoNaY	$CoCl_2$ (Merck)	3.9

of 6 K/min to 673 K. After cooling to 573 K in Ar, the catalyst was sulfided in 10% H_2S/H_2 for 2 h. MoS_2 powder (Janssen Chimica, 99+%, B.E.T. surface area 3.9 m^2/g) was heated to 673 K at a rate of 6 K/min in the sulfidation mixture and kept there for 2 h.

Catalysts will be denoted as follows: TM/S(T), where TM stands for the transition metal(s), S for the support, and T the sulfidation temperature. Cobalt-exchanged NaY is denoted CoNaY(573 K), while the MoS_2 powder is denoted MoS_2(673K).

Thiophene HDS Reaction

Activity measurements were carried out in an atmospheric single-pass microflow reactor with an internal diameter of 4 mm. Gasified thiophene (Acros, >99%) was obtained by passing hydrogen (Hoekloos, purity 99.95% additionally led through a gas-clean filter system to remove traces of oxygen, water, and hydrocarbons) through the liquid in a saturator equipped with a cooler that was kept at a constant temperature of 280 K. The required thiophene concentration was obtained by diluting this flow with pure hydrogen. The reactor packing consisted of an amount of catalyst diluted with inert carbon (125–250 μm) to achieve plug flow conditions. The thiophene HDS reaction temperature was 673 K. Samples were analyzed by a gas chromatograph (Hewlett Packard 5890 series II equipped with a Chrompack CP-SIL 5 CB column). For the calculation of the rate constant (k_{HDS}) first-order kinetics in thiophene were assumed (21). For a series of six Co/C catalysts with varying Co loading the activity was measured under differential conditions allowing the calculation of quasi-turnover frequencies.

H_2–D_2 Equilibration Apparatus

The H_2–D_2 equilibration activities were measured using a recirculation reactor set-up schematically shown in Fig. 1. A membrane pump (pump flow rate: 1 L/min at 1 bar) is used to recirculate gases in the recirculation loop. In order to achieve a flow rate of 50 Nml/min the pump inlet and
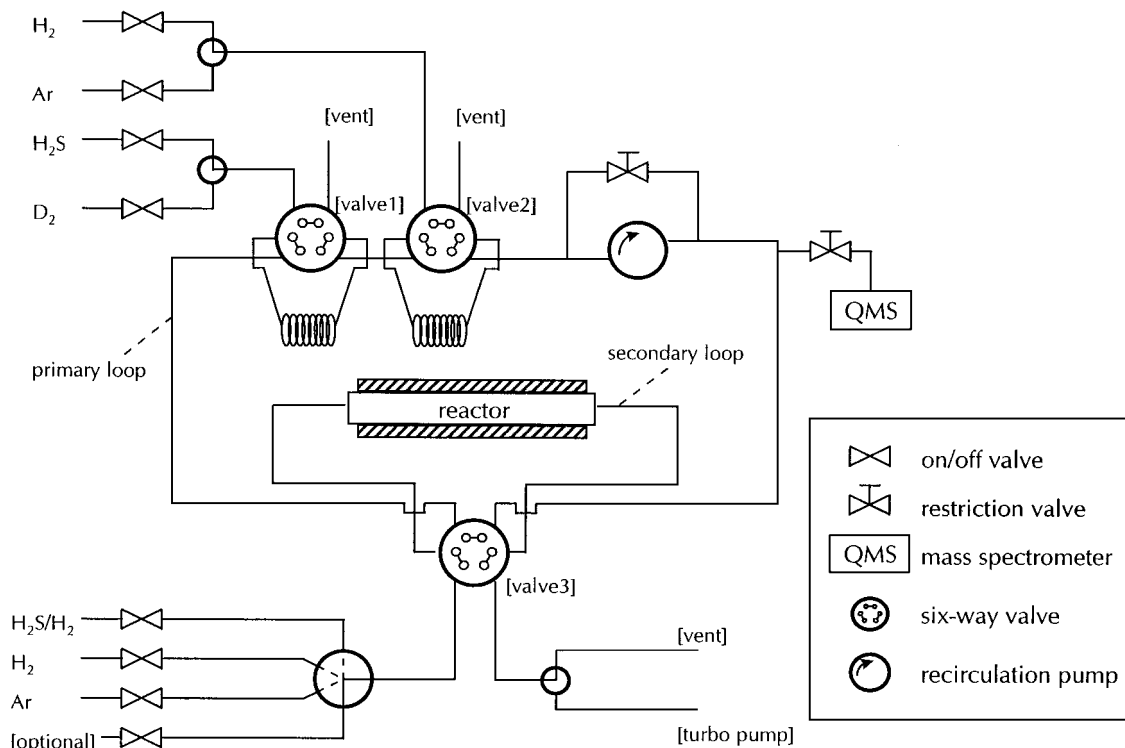
FIG. 1. Schematic layout of recirculation apparatus.

outlet were short-circuited with a restriction valve. Initially, the primary recirculation loop ($V_{loop} = 213$ ml) is filled with Ar (Hoekloos, purity 99.99% additionally led over a BTS catalyst at 398 K in order to remove traces of oxygen). By switching the six-way valves 1 and 2, samples (10 ml) of H₂ (Hoekloos, purity 99.95%), D₂ (Praxair, purity 99.8%), or H₂S (Praxair, purity 99.8%) can be introduced into this primary loop. During this sampling, catalyst pretreatment takes place in the secondary loop. After the final pretreatment step the reactor ($V_{reactor} = 17$ ml) is evacuated by a turbo molecular drag pump (vacuum better than 10^{-6} bar). The reaction is started by switching six-way valve 3: the gas present in the primary loop is quickly distributed over the evacuated secondary loop. The initial primary loop pressure is $1.11.10^2$ kPa. When the reaction has been started the total system pressure is 1.07×10^2 kPa.

Continuous on-line analysis of all gas-phase components was performed by a quadropole mass spectrometer (Balzers QMG 200M system) equipped with a secondary electron multiplier operating at 1200 V. During a typical experiment the gas flow rate into the mass spectrometer was so low that the decrease in system pressure was less than 1%. Mass spectra were collected every 0.5 min. Gas-phase concentrations of H₂, D₂, HD, and H₂S were calculated after calibration with the individual pure gases. The deuterium distribution in H₂S was determined by deconvolution of the peaks in the range m/e = 32–38.

H₂–D₂ Equilibration Reaction

The primary loop is filled with 6.5 kPa H₂ and 6.5 kPa D₂. In some experiments H₂ was left out or (partially) replaced by H₂S. After sulfidation of the catalyst, the H₂S/H₂ flow was replaced by Ar (flow rate 60 Nml/min). The catalyst was cooled or heated to the equilibration reaction temperature (423 K) and kept there for 1 h. The reaction was started after the reactor was evacuated.

RESULTS AND DISCUSSION

Thiophene Hydrodesulfurization

In Table 2 the initial thiophene HDS activities of the different catalysts are shown both on a per kilogram of

TABLE 2

Initial First-Order Thiophene HDS Rate Constants
($T = 673$ K; 4% Thiophene)

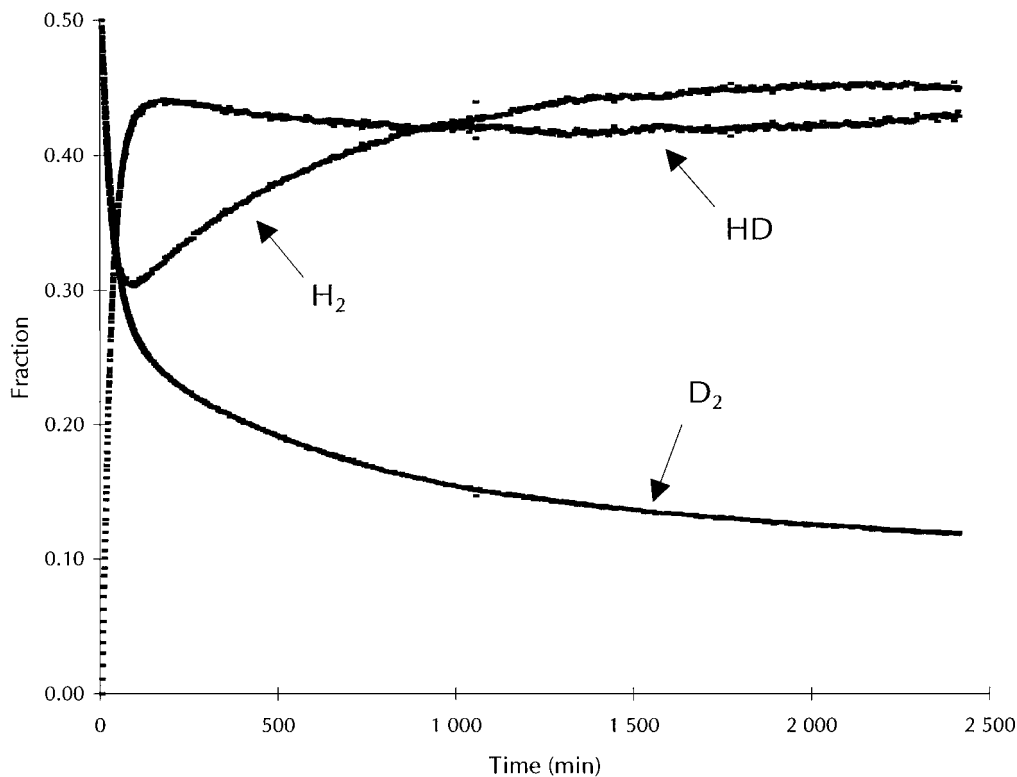| Catalyst	Activity (10^{-3} m³/kg$_{cat}$ · s)	Activity (L/mol Co · s)
MoS₂ powder	0.4	—
Mo/C	11.8	—
Co/C (673 K)	24.7	21.3
CoNaY (573 K)	17	25
CoMo/C	74	362

FIG. 2. H_2–D_2 equilibration ($T = 423$ K; $P_{H_2} = P_{D_2} = 6.5$ kPa): gas-phase H_2, D_2, and HD fraction as a funcion of reaction time over CoMo/C(673 K).

catalyst basis as well as on a per mol of Co basis. CoMo/C(673 K) is about six times more active than the unpromoted Mo/C(673 K), a promoter effect often encountered in the literature (22). The activities of Co/C(673 K) and CoNaY(573 K) are quite comparable, while the activity per mole of Co of CoMo/C(673 K) is much higher than that of Co/C(673 K) and CoNaY(573 K). As expected, the low-surface-area MoS_2(673 K) has a very low thiophene HDS activity.

H_2–D_2 Equilibration

Figure 2 shows the results of a typical H_2–D_2 equilibration experiment over CoMo/C(673 K). The gas-phase fractions of H_2, D_2, and HD are plotted against the reaction time. The initial gas pressures of hydrogen and deuterium were both 6.5 kPa. The reaction was performed at 423 K. It is important to note that Mo/C(673 K) shows qualitatively the same behavior. Initially, the fraction of HD increases at the expense of H_2 and D_2. However, after a reaction time of 100 min an increase in the H_2 fraction is observed, while an equilibrium state is reached after approximately 2400 min. The fact that in this equilibrium state the H_2 fraction exceeds the D_2 fraction indicates that initially exchangeable hydrogen species were present in our closed system. Apparently, these hydrogen species are present on the catalyst.

When it is assumed that the ratio of hydrogen to deuterium species is uniform in the reactor (i.e., in the gas phase and on the catalyst) at equilibrium, the total amount of exchangeable hydrogen species initially present on the catalyst (H_0) can be calculated from the final hydrogen to deuterium ratio in the gas phase

$$\left(\frac{H}{D}\right) = \left(\frac{2H_{2g} + H_0}{2D_{2g}}\right)_{t=0} = \left(\frac{2H_{2g} + HD_g}{2D_{2g} + HD_g}\right)_{equilibrium},$$

where the subscript g stands for the molar amount in the gas phase and the subscript 0 stands for the molar amount on the catalyst.

In this case one calculates the number of exchangeable hydrogen atoms, H_0, to be 7.0×10^{-3} mol H/g catalyst. There are two possible sources of hydrogen: (i) hydrogen associated with the sulfided phase and (ii) hydrogen present at the support surface. Several studies have been devoted to the behavior of H_2 over sulfide catalysts, mostly dealing with hydrogen sorption on unsupported MoS_2 and supported MoS_2 (23–28). For instance, Komatsu and Hall (27) found that hydrogen sorbs both on unsupported MoS_2 (H/Mo = 0.045) and on alumina-supported MoS_2 (H/Mo = 0.47). The nature of this sorbed hydrogen is unknown, although there seems to be general agreement that at least a part is present as SH^- groups at the MoS_2 edges (23, 27, 29). Molecular

orbital calculations on small model clusters for MoS_2 by Anderson *et al.* (30) have shown that hydrogen can dissociate heterolytically to form a hydride group and an edge SH group. There is a small barrier for migration of H atoms from edge S atoms to basal plane S atoms, which was already proposed by Wright *et al.* (23). A maximum amount of H atoms associated with basal plane sulfur was calculated to be $H_{6/7}MoS_2$. Badger *et al.* proposed the intercalation of H_2 into the chalcogenide sheets of MoS_2 (31).

In consequence, it seems fair to conclude that the high value for H_0 (which amounts to $H_0/Mo = 11$ on a per mol Mo basis) cannot be attributed solely to H atoms associated with the sulfided phase. Moreover, the pretreatment procedure, viz., Ar purging and evacuation, probably results in the desorption of most of the sorbed hydrogen. Based on the above-mentioned considerations, we believe that at least the larger part of this excess of H atoms cannot originate from the sulfided phase. Apparently, these H atoms are associated with the carbon support surface. The surface of activated carbon contains different kinds of oxygen-containing functionalities such as hydroxyl and carboxyl groups as well as CH_2 and CH_3 groups (32, 33). The fact that H_0 is of the same magnitude for all carbon-supported catalysts (Table 3) supports this proposition. MoS_2(673 K) contains only a small amount of hydrogen ($H_0/Mo = 0.21$), which might be attributed to intercalated hydrogen or hydrogen adsorbed on the basal planes. This result indicates that the contribution of H atoms originating from the sulfide phase is small compared to the number of exchangeable H atoms of the support.

The same findings were reported previously for alumina-supported (Ni)Mo sulfide catalysts by Thomas *et al.* (34, 35). Apparently, the exchange between H atoms of the support via the sulfide is a general phenomenon for supported sulfide catalysts. The H_0 value found for alumina-supported NiMo sulfide (34), i.e., 5×10^{14} mol H/cm^2, is on the same order of magnitude as the values found for our carbon support. Also, the H/Mo value for bulk MoS_2 reported in that paper (H/Mo = 0.24) agrees very well with our value (H/Mo = 0.21), stressing the reliability of the method. The carbon support itself was inert in the H_2–D_2 equilibration reaction, which means that the sulfide phase plays an essential role in the exchange of H atoms originating from the support surface. This process is generally referred to as spillover (10–12, 25, 26, 28). Summarizing, it appears that

TABLE 4

Activity in H_2–D_2 Equilibration Reaction
($T = 423$ K; $P_{H_2} = P_{D_2} = 6.5$ kPa)

Catalyst	Initial rate of HD formation (mol/mol · h)
MoS_2(673 K)	0.003^a
Mo/C(673 K)	2.8^a
CoMo/C(673 K)	9.1^a; 30.3^b
Co/C(373 K)	0.15^b
Co/C(373 K, H_2)	0.19^b
Co/C(673 K)	0.02^b
CoNaY(573 K)	0.11^b

[a] Per mol Mo.
[b] Per mol Co.

H_2 and D_2 dissociatively adsorb on the sulfide phase and that concomitant HD desorption takes place. Furthermore, there appears to be an exchange of D atoms adsorbed on the sulfide phase (D_{sulf}) with H atoms at the support surface (H_{supp}) via spillover.

As a measure for the activity of the various catalysts, the initial rate of HD formation was calculated (see Table 4). It is clear that CoMo/C(673 K) has the highest activity while the catalysts containing only Co have very poor activity. The activity of the MoS_2(673 K) is lowest, in line with its very low surface area. CoMo/C(673 K) is about three times more active than Mo/C(673 K). While the plot of fractions against reaction time for Mo/C(673 K) is qualitatively similar to the experiment with CoMo/C(673 K), the plot for Co/C(373 K) (Fig. 3a) is clearly different. Evidently, the initial rate of HD formation on this catalyst is low but after a short time the reaction accelerates and becomes accompanied by a release of hydrogen sulfide species into the gas phase due to the partial reduction of cobalt sulfide. Approximately one S atom per cobalt atom is removed by this reduction. In Fig. 3b the evolution of hydrogen (deuterium) sulfide species (H_2S, HDS, and D_2S) can be found. Clearly, the initial rate of D_2S formation is much lower than that of H_2S. This can be attributed to an initially lower D_{sulf} compared to H_{sulf}, since the dissociation rate constant for D_2 is approximately 15 times lower than that for H_2 under the conditions applied. The two determining factors for this difference are the shift in zero point energy ($\nu(H_2) = 4159$ cm^{-1}; $\nu(D_2) = 2149$ cm^{-1}) and the difference in rotational moment.

The initial activity of Co(673 K)/C is one order of magnitude lower than that of Co(373 K)/C, which can be explained by the bulkier and thus less dispersed Co_9S_8-type phase. Furthermore, only a very small evolution of hydrogen sulfide species for Co(673 K)/C was observed, which corresponded to about 0.01 S/Co as was also the case for Mo/C(673 K) and CoMo/C(673 K). This indicates that only a light reduction takes place or that this release can be attributed to chemisorbed hydrogen sulfide. As freshly
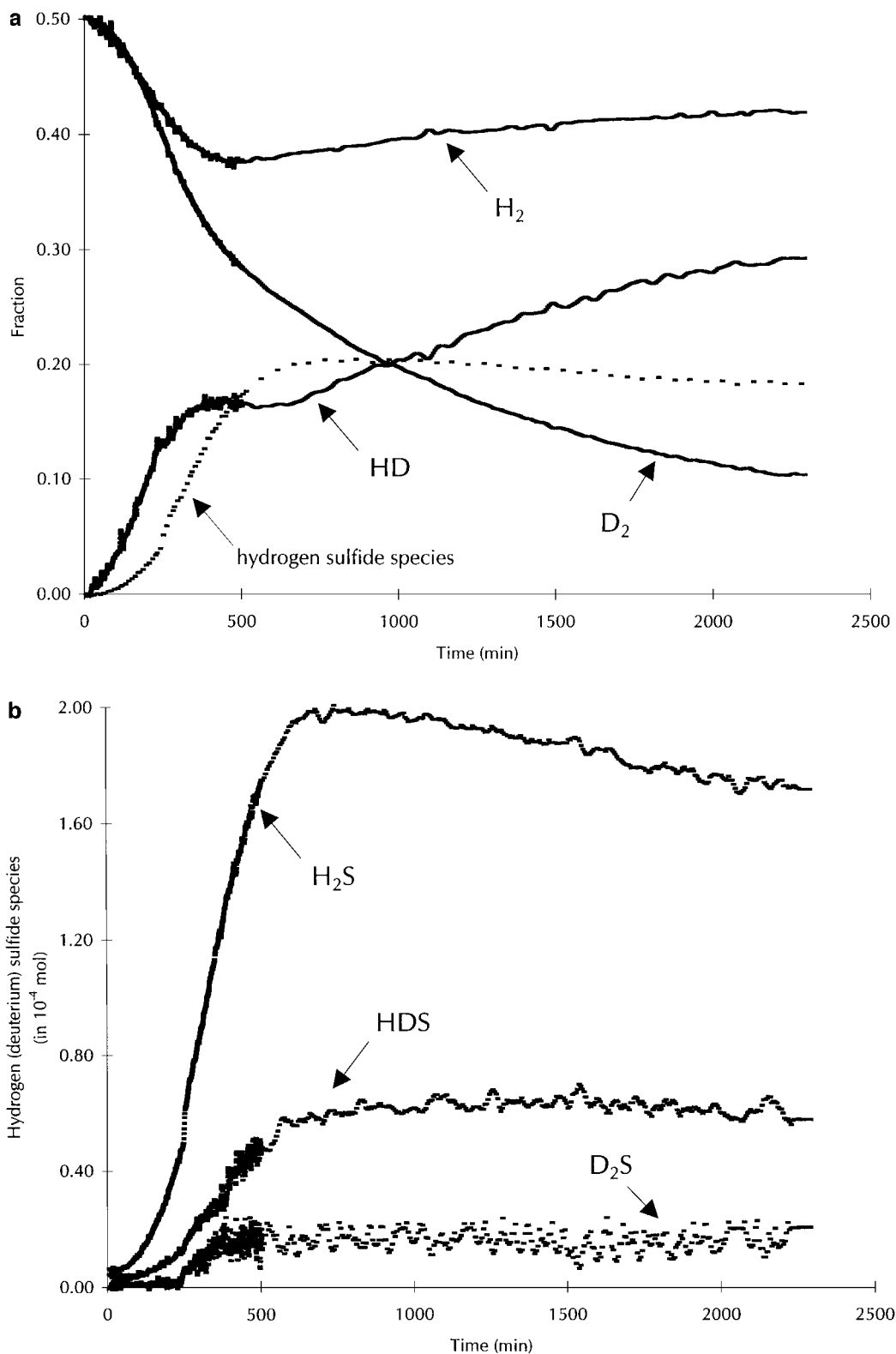
TABLE 3

Number of Exchangeable Support H Atoms (H_0)

Catalyst	H_0 (mol H/g)	H atoms/cm^2 support
Mo/C(673 K)	6.3×10^{-3}	3.2×10^{14}
Co/C(373 K)	8.2×10^{-3}	4.2×10^{14}
CoMo/C(673 K)	7.0×10^{-3}	3.5×10^{14}

FIG. 3. H$_2$–D$_2$ equilibration ($T = 423$ K; $P_{H_2} = P_{D_2} = 6.5$ kPa) over Co/C(373 K): (a) gas-phase H$_2$, D$_2$, and HD fractions; (b) amount of H$_2$S, D$_2$S, and HDS produced as a function of reaction time.

sulfided Co/C(373 K) is not stable under our H_2–D_2 reaction conditions, the activity of a reduced Co/C(373 K) was measured. This catalyst [Co/C(373 K, H_2)] was obtained by purging Co/C(373 K) for 1 h in flowing Ar after a regular experiment. In this way, one sulfur atom per Co was removed as H_2S. Subsequently, a new H_2–D_2 experiment was carried out [Table 4; Co/C(373 K, H_2)]. Indeed, the activity is approximately 30% higher than that of Co/C(373 K), while little hydrogen sulfide production was observed.

EXAFS measurements by Crajé et al. (9) have shown that the first two coordination shells of cobalt (Co–S and Co–Co) are similar for Co/C(373 K) and CoMo/C(673 K) and essentially differ from the spectra for Co/C(673 K). The coordination number for Co–S (N_{Co-S}) was found to be 6.0 in the case of Co(373 K)/C and 5.1 in the case of CoMo/C(673 K), while N_{Co-S} was 3.6 for Co/C(673 K), indicating the presence of a bulky Co_9S_8-type phase. Apparently, the sixth S atom around Co in Co/C(373 K) is easily removed by reduction with H_2 under the conditions applied. The sixth S atom coordinating Co in CoMo/C(673 K) is absent, because it is less stable or possibly removed as H_2S during the pretreatment steps. In addition, it is found that CoNaY(573 K) shows no significant release of hydrogen sulfide during H_2–D_2 equilibration, which is in line with a Co–S coordination number of 5 for this catalyst (19).

Quadrupole splitting (QS) values of the "Co–sulfide" doublet for catalysts equivalent to ours are summarized in Table 5. It can be concluded that the thiophene HDS activity of the catalysts containing only Co increases with increasing QS value. It is important to note that a high QS value is related to highly dispersed and/or disordered Co sulfide particles. For these monometallic sulfides, we find a clear-cut relation between the H_2–D_2 equilibration activity and the QS value. It is tempting to interpret the QS value as a measure for the dispersion. However, EXAFS measurements (19) have shown that there is no Co–Co coordination in CoNaY(573 K), suggesting the presence of CoS_x species with one Co atom. It follows that in addition to effects of particle size and ordering of the sulfide phase changes in

the local electronic structure, exerted by, e.g., the choice of support, influence QS. As pointed out by Vissenberg (36), one important role of the acidic protons in sulfided CoNaY(573 K) is to keep the very small CoS_x clusters in a dispersed form inside the zeolite micropores. This may involve a direct bonding of the CoS_x species to the acidic protons.

The comparable QS value for Co/C sulfided at 373 K and for sulfided CoMo/C points to similar small CoS_x clusters in both systems. This was taken as support for the idea that the high activity of CoMo/C is due to the high dispersion of Co (7). A direct evaluation of the thiophene HDS activity of Co/C(373 K) is not possible, since the small CoS_x clusters convert to a bulky Co_9S_8-type phase at typical hydrotreating reaction temperatures. However, the H_2–D_2 equilibration activities measured at 423 K permit a direct comparison between Co/C(373 K) and CoMo/C(673 K). Despite the above-mentioned structural similarities, it is clear that Co/C(373 K) is much less active than CoMo/C(673 K). Therefore, we conclude that the synergy observed for CoMo/C(673 K) in H_2–D_2 equilibration cannot be explained by the high dispersion of Co. The results indicate that the high activity of CoMo/C(673 K) is related to the chemical properties of both Co and Mo.

Moreover, the low activity of catalysts containing only the Co component can be taken as a strong argument against the remote control model: under the conditions applied, the sulfide phase present in Co/C(373 K) and Co/C(673 K) generates very little spillover H atoms, while a clear synergetic effect is observed in CoMo/C(673 K). This clearly contradicts the importance of Co sulfide (donor) to the creation of vacancies on MoS_2 (acceptor) as suggested by Delmon (10–12). In conclusion, the high activity in CoMo/C(673 K) must be related to a close contact between Co and Mo in line with the proposals for a Co–Mo–S-type phase.

The quasi-turnover frequencies (QTOF) for thiophene HDS, defined as the number of moles of thiophene converted per mole of total Co per hour, of a series of six Co/C catalysts are presented in Fig. 4. Extrapolation of 1/QTOF versus the loading to zero loading as previously described by Vissers et al. (6) leads to an intrinsic activity of 165 mol thiophene/mol Co · h, which is substantially lower than the value found for CoMo/C (436 mol thiophene/mol Co · h). This result is essentially different from that obtained by Vissers et al. (6). They concluded that the intrinsic activity of Co sulfide in Co/C is equivalent to the activity of Co sulfide in CoMo/C. The reason for this difference lies in the differential conditions applied in the present study, which allow a proper calculation of QTOF, while Vissers et al. (6) calculated QTOF values on the basis of first-order kinetics. Furthermore, Bouwens et al. (37) have shown that the preparation method used by Vissers et al. (6)—sequential impregnation of Mo and Co—leads to a CoMo catalyst with Co present in different phases, i.e., in both a Co–Mo–S-type

TABLE 5

Q.S. Values in mm/s (±0.03 mm/s) of the "Co-Sulfide" Doublet

Catalyst	Sulfidation temperature	Q.S. (mm/s)
Co/C	373 K	1.08[a]
Co/C	673 K	0.39[a]
CoMo/C	673 K	0.88[a]
CoNaY	573 K	0.63[b]

[a] The spectral contribution of the Co-sulfide doublet is 100%; loading: Co(4.3)/C and Co(2.25)Mo(6.84)/C; data are from Crajé et al. (4).

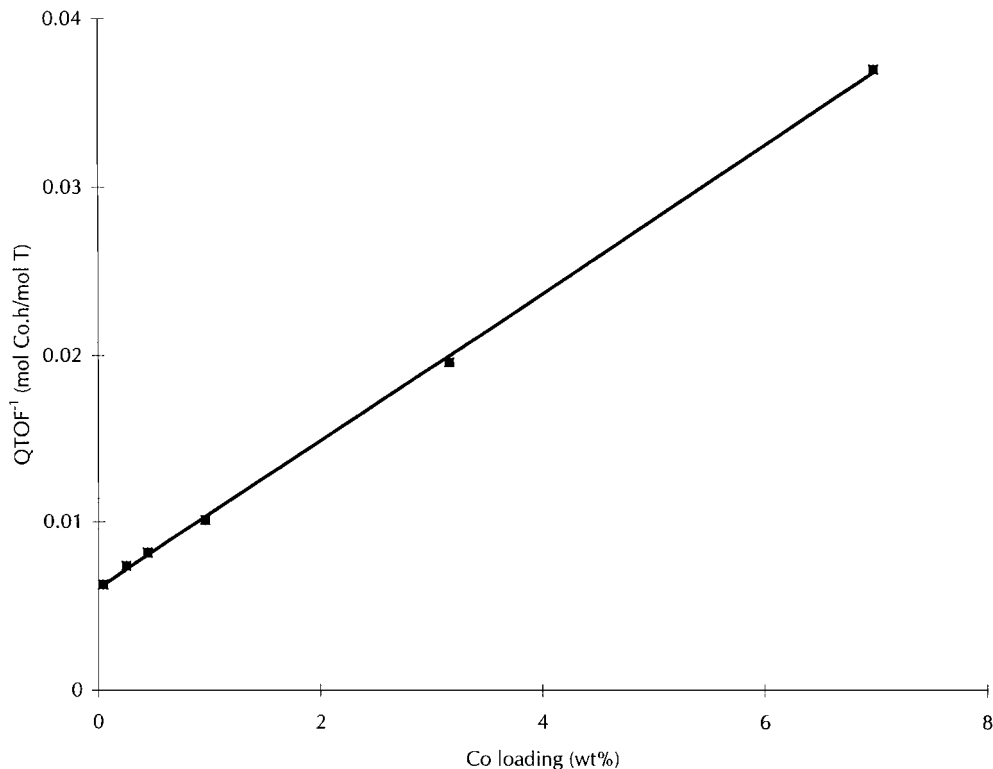[b] The spectral contribution of the Co-sulfide doublet is 69%; data are from De Bont et al. (19).

FIG. 4.   1/QTOF versus the Co loading of the various Co/C catalysts (thiophene HDS; 4% thiophene in H_2; $T = 673$ K).

phase and a Co_9S_8-type phase. The mono-atomically dispersed CoS_x particles in CoNaY(573 K) have a lower activity than the small CoS_x particles in Co/C with low Co loadings. This strongly suggests that there exists an optimal size of CoS_x particles for the hydrodesulfurization of thiophene. In conclusion, the thiophene HDS acitivity per mol of Co in CoMo/C(673 K) is much higher than that in the catalysts containing only Co, stressing again the importance of the presence of a unique phase containing both Co and Mo.

The present results provide the important insight that neither the effect of high dispersion of CoS_x particles nor spillover effects can explain the synergy between Co and Mo in CoMo/C(673 K). Apparently, Co and Mo in a specific configuration are mandatory for high activity. The edge-decoration models (37, 38) based on the Co–Mo–S model provide such a configuration. However, Crajé *et al.* (4) already pointed out that the idea of Co ions being present at well-defined positions of MoS_2 is in contrast with a varying QS value as a function of both sulfidation temperature and Co/Mo ratio.

The pivotal question still relates to a satisfactory explanation for the observed synergy. On the basis of MES measurements (4) one concludes that the local (electronic) structures of Co in Co/C(373 K) and CoMo/C(673 K) are similar. These small CoS_x particles have a low activity in activating H_2. Therefore, an explanation may be provided by the higher reactivity of the sulfur atoms that bridge between the Mo^{4+} and the Co^{2+} ions compared to the bridging sulfur atoms between two Mo^{4+} ions in MoS_2. This is in line with the higher reactivity of CoMo/C(673 K) than that of Mo/C(673 K): the lower oxidation state of Co^{2+}, which can be thought to replace a Mo^{4+}, leads to a less stable and thus more reactive bridging S atom. The work of Byskov *et al.* (14) agrees well with this model, while both experimental work (39) and theoretical work (13, 40) underscore the crucial role of these S atoms in the catalytic cycle. Interestingly, recent work of Curtis and Druker (41) has demonstrated that carbonyl and cyclopentadienyl ligand stabilized "$Co_2Mo_2S_3$" clusters can activate C–S bonds. An initially threefold coordinated bridging sulfur atom becomes twofold coordinated upon adsorption of thiophene on the cluster. The concept of latent vacancies was introduced, which may also be applicable to a Co–Mo–S-type site.

All things considered, we tentatively conclude that the generation of a unique Co–Mo–S-type phase is the basis for the synergetic effect not only in the H_2–D_2 equilibration but also in many types of hydrotreating reactions.

D_2 Exchange

In Fig. 5 the results are shown after exposure of CoMo/C(673 K) to D_2 (initial D_2 partial pressure: 6.5 kPa). The
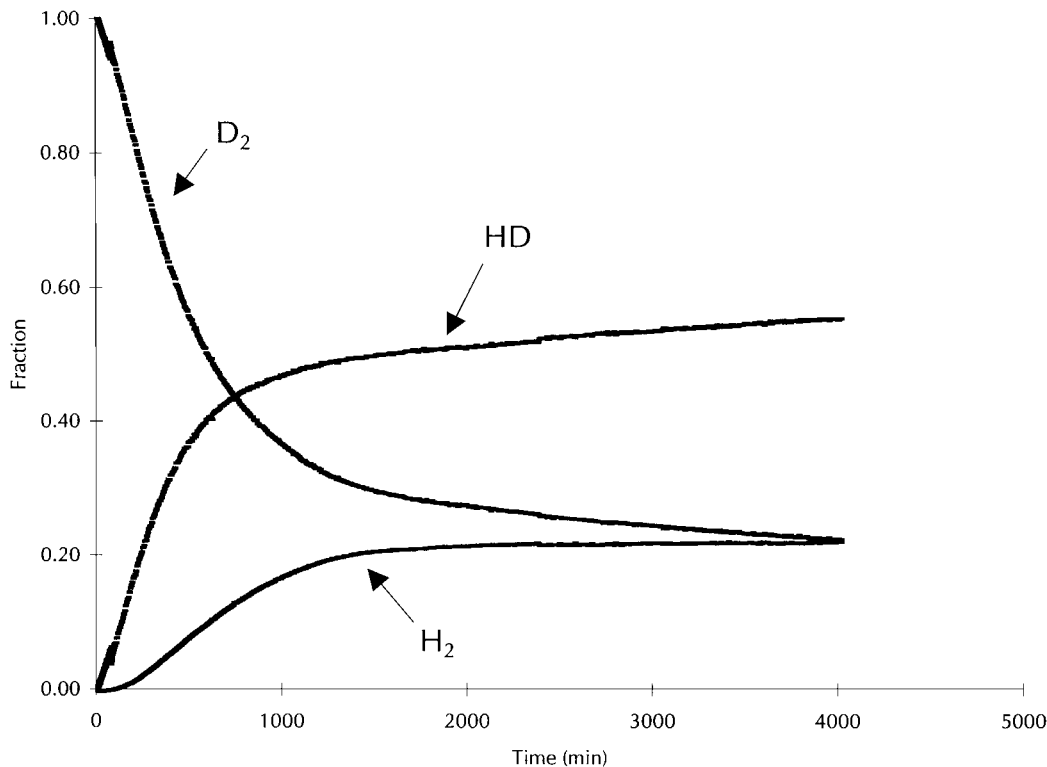
FIG. 5. D_2 exchange ($T = 423$ K; $P_{D_2} = 6.5$ kPa): gas-phase fractions as a function of reaction time over CoMo/C(673 K).

initial rate of HD formation is much lower than encountered in the H₂–D₂ equilibration experiments. This shows that the exchange process between D_{sulf} and H_{supp} is slow compared to the rates for adsorption and desorption. While HD is formed as an initial product, H₂ is formed as a secondary product. In Table 6, the rates for the D₂ exchange experiments over Mo/C(673 K) and CoMo/C(673 K) are presented. Most striking is the small difference in initial HD formation rate between the two catalysts, which suggests that there is no large promoter effect for the exchange process with the support hydrogen atoms (H_{supp}). The H_0 values for these experiments correspond well with the values obtained from the H₂–D₂ equilibration experiments.

The low initial HD formation rate in the D₂ exchange experiments compared to the H₂–D₂ equilibration experiments indicates that the rate in the D₂ exchange experiments is controlled by the exchange of D_{sulf} and H_{supp}. From the much higher activity measured in the H₂–D₂ experiments one concludes that the adsorption/desorption rates on the sulfide phase are fast compared to the exchange rate with support hydrogen atoms (H_{supp}).

Effect of H₂ and D₂ Partial Pressure

In Table 7 the activities of Mo/C(673 K) and CoMo/C(673 K) are shown as a function of the H₂ and D₂ partial pressures. From the observed dependence of the initial HD formation rate for CoMo/C(673 K) as a function of H₂ and D₂ partial pressure, one concludes that the rate is proportional to the coverages of H and D atoms on the sulfide

TABLE 6

Activity Data for D₂ Exchange Experiments
($T = 423$ K; $P_{D_2} = 6.5$ kPa)

Catalyst	Initial rate of formation (mol/mol Mo · h)		Exchangeable H atoms (mol H/g)
	HD	H₂	
Mo(673 K)/C	0.22	0.00	7.3×10^{-3}
CoMo(673 K)/C	0.29	0.00	7.5×10^{-3}

TABLE 7

Activity Data for Mo/C(673 K) and CoMo(673 K) as a Function of
H₂ and D₂ Partial Pressure ($T = 423$ K)

Catalyst	P_{H_2} (kPa)	P_{D_2} (kPa)	Initial rate of HD formation (mol/mol Mo · h)
Mo/C(673 K)	3.25	3.25	0.7
	6.5	6.5	2.7
CoMo/C(673 K)	3.25	3.25	4.4
	6.5	6.5	9.1

phase. In this case, the rate-limiting step must be a surface reaction that is either the migration of H and D species or the recombinative desorption of HD. On the contrary, the rate for Mo/C(673 K) is clearly first order in H_2 and D_2 partial pressure. Apparently, the rate-limiting step is now the adsorption of H_2 and D_2. This may indicate that in addition to atomic H and D atoms, molecularly adsorbed H_2 (or D_2) is present in Mo/C(673 K).

It follows that CoMo/C(673 K) is a more efficient catalyst for activating H_2 than Mo/C(673 K) under the conditions applied, which may relate to the unique sulfur reactivity as discussed above.

H_2S–D_2 Exchange

To shed light on the catalytic behavior of H_2S for hydrotreating catalysis over CoMo/C(673 K), the isotopic exchange between H_2S and D_2 was studied. In Fig. 6 the fractions of H_2, HD, and D_2 for CoMo/C(673 K) (Fig. 6a) and the deuterium distribution in H_2S (Fig. 6b) are plotted against reaction time. Note that the exchange between equimolar amounts of H_2S and D_2 was studied and that the total gas-phase fraction of H_2S, D_2S, and HDS as well as H_2, D_2, and HD is taken as unity. The activity data are presented in Table 8, experiment IV. As can be seen there is an isotopic exchange between H_2S and D_2, resulting in the formation of HD, H_2, HDS, and D_2S. In contrast to the D_2 exchange experiment, direct formation of H_2 is observed, which points to a fast exchange between the H atoms of adsorbed H_2S and the adsorbed D atoms to form HD, H_2, HDS, and D_2S. While both HDS and D_2S appear as initial products, it is peculiar that the initial rate of formation of D_2S is very low. Moreover, when the balance for H and D atoms is calculated, one finds that initially 6.9 mol H/mol · h are evolved into the gas phase while the same amount of deuterium atoms disappear. It is clear that the exchange of D_{sulf} with H_{supp} is accelerated by the presence of H_2S. Indeed, from Fig. 6a it follows that total equilibration is already reached after 500 min, while in earlier experiments (Fig. 2) this process took longer than 2000 min. One possi-

ble explanation is the migration of D atoms via HDS and D_2S from the sulfide surface to the support surface via the gas phase as proposed by Thomas et al. (35). However, the number of D atoms involved in HDS and D_2S formation amounts to 2.3 mol D/mol · h, which is substantially lower than the rate at which D atoms are initially incorporated into the support surface. This was also outlined by Bianchi et al. (42) describing the effect of H_2O in the case of spillover phenomena over Pt/Al$_2$O$_3$ and silica, while Stumbo et al. (43) suggested that the increase in spillover rate by H_2S over CoMo/SiO$_2$ can be explained by the creation of new sites and a new pathway for spillover. Nakamura et al. (44) proposed that upon adsorption of H_2S an SH group and one spillover H atom are formed.

Another possible pathway is derived from the work by Topsøe and Topsøe (45). They showed that hydrogen bonding between SH groups on the sulfide phase and surface alumina hydroxyl groups led to a new IR band assigned to more acidic surface hydroxyl groups. It was proposed that these SH species are generated by dissociative H_2S adsorption. This may be a facile pathway for the spillover process of D_{sulf}. The rate of exchange is proportional to the number of these species and thus related to the H_2S partial pressure. Moreover, this can explain the smallness of the difference in activity for Mo/C(673 K) and CoMo/C(673 K) in the D_2 exchange experiment (see Table 6), since the type of metal on which these terminal SH groups are bonded may not be very important.

In Table 8 an overview of the relevant experiments regarding the effect of H_2S is presented. In experiment II the H_2 partial pressure is lowered compared to experiment I, resulting in a lower initial HD formation rate. Again, the rate is proportional to the square root of the H_2 partial pressure and thus proportional to H_{sulf} (vide supra). Experiment III essentially differs from experiment II by the admixture of H_2S, while the partial pressures of both H_2 and D_2 are kept constant. The lower initial HD formation rate points to competitive adsorption of H_2S and H_2 (or D_2). Since it is generally accepted that H_2S adsorbs on sulfur vacancies as originally proposed by Lipsch and Schuit (46), i.e., coordinatively unsaturated sites, we conclude that dissociative H_2 adsorption leads to the formation of at least one metal hydride and most probably an SH group. These results are in good agreement with the conjecture put forward by Thomas et al. (34). This heterolytic dissociation of H_2 on sulfide surfaces was proposed previously (31, 47), whereas experimental indications for hydride formation are scarce (48). Goodenough (49) proposed the homolytic dissociation of H_2 on an S_2^{2-} center, which appears to be in contrast with our experimental results. The initial HDS formation rate in experiment IV is a factor of 5 higher than that in experiment III: the absence of H_2 results in a higher D_{sulf}, leading to an increased exchange between H atoms of H_2S and D atoms. Although we cannot determine the

TABLE 8

Activity Data for Experiments Using Mixed Feeds of H_2, D_2, and H_2S (Catalyst: CoMo(673 K)/C; Temperature: 423 K)

Experiment	Partial pressures (kPa)			Initial rate of formation (mol/mol Mo · h)			
	H_2	D_2	H_2S	H_2	HD	D_2S	HDS
I	6.5	6.5	0	—	9.1	—	—
II	3.25	6.5	0	—	6.0	—	—
III	3.25	6.5	3.25	—	5.3	0.05	0.36
IV	0	6.5	6.5	2.4	4.1	0.2	1.9
V[a]	6.5	6.5	0	—	7.5	—	—

[a] Cooled to reaction temperature in sulfidation mixture.
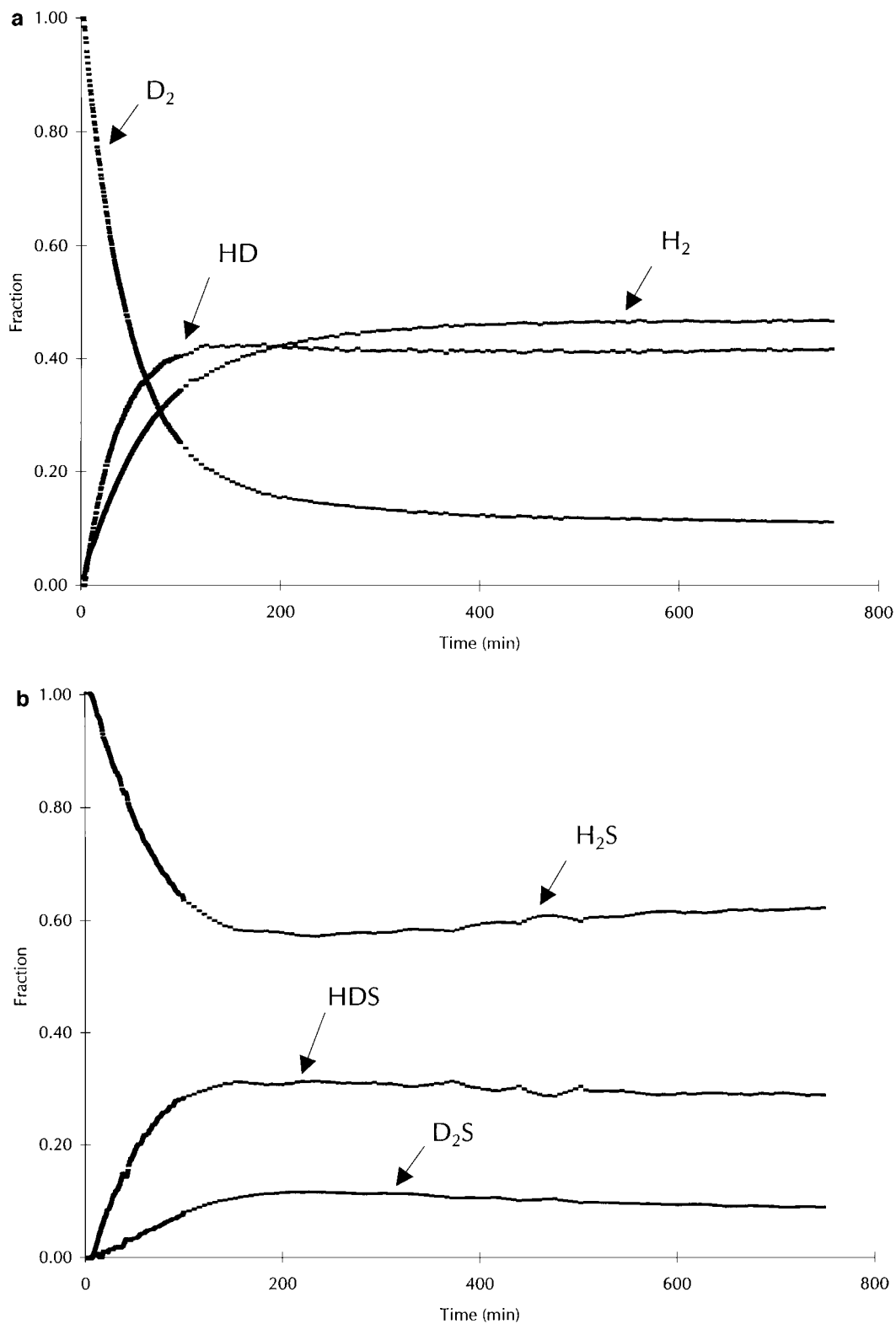
FIG. 6. H$_2$S–D$_2$ exchange ($T = 423$ K; $P_{H_2S} = P_{D_2} = 6.5$ kPa) over CoMo/C(673 K): (a) gas-phase H$_2$, D$_2$, and HD fractions; (b) gas-phase H$_2$S, D$_2$S, and HDS fractions as a function of reaction time.
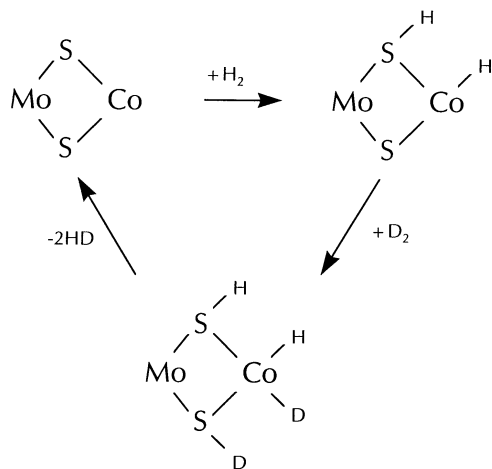
FIG. 7. Schematic representation of catalytic H_2–D_2 equilibration over a "Co–Mo–S"-type site.

mode of adsorption of H_2S, the widely accepted heterolytic dissociation of H_2S (50) can explain the observed exchange processes. As already indicated by Thomas *et al.* (34), it appears that there exists a common mode for dissociation of H_2 and H_2S, i.e., heterolytic dissociation.

From the low rate of exchange between D_{sulf} and H_{supp} in the absence of H_2S, we conclude that SH groups formed via heterolytic H_2 dissociation are inactive in promoting the spillover process. This means that they are different from the SH groups formed by heterolytic H_2S dissociation. Accordingly, we propose that H_2 dissociates heterolytically to form a Co hydride and a bridging SH group as depicted in Fig. 7. After heterolytically dissociative D_2 adsorption, HD desorption can take place. In this model the exchange takes place after dissociation of H_2 and D_2 at a single Co center. However, the dissociation might also take place at discrete centers concomitant with migration of H (D) atoms on the sulfide surface (33).

When no H_2S is present in the gas phase the number of terminal SH groups is low, leading to a low rate of exchange with the H atoms at the support surface. However, when H_2S is present the spillover process will accelerate due to an increase in the number of terminal SH groups. H_2S competitively adsorbs on coordinatively unsaturated sites with H_2 and D_2, thus lowering H_{sulf} and D_{sulf}. Consequently, this leads to a lower initial HD formation rate. The hydrogen bonding between terminal SH groups and surface functional groups and the subsequent exchange is visualized in Fig. 8. It is important to note that the heterolytic dissociation of H_2S leads to two SH groups: one SH group bound between Co and Mo, which is believed to be more strongly bound (39) than the second SH group, which is terminally bound to the Co center.

The low activity encountered in the D_2 exchange experiment can now easily be explained by the small number of terminal SH groups resulting in a low spillover rate. In experiment V (Table 8) the catalyst was cooled to reaction temperature in the sulfidation mixture instead of Ar. It appears that the resulting initial rate of HD formation is lower than in experiment I, showing that the lower purge temperature results in a lower coordinative unsaturation. Furthermore, the time to reach the equilibrium state was found to be somewhat shorter, which is in line with the increase of terminal SH groups on the sulfide surface.

CONCLUSIONS

By using the H_2–D_2 equilibration reaction at 423 K the catalytic activity of structurally analogous CoS_x particles, i.e., in Co/C (373 K) and in CoMo/C (673 K), could be meaningfully compared for the first time. From the much higher activity in the bimetallic catalyst, it is concluded that this increased activity cannot be explained by the high dispersion
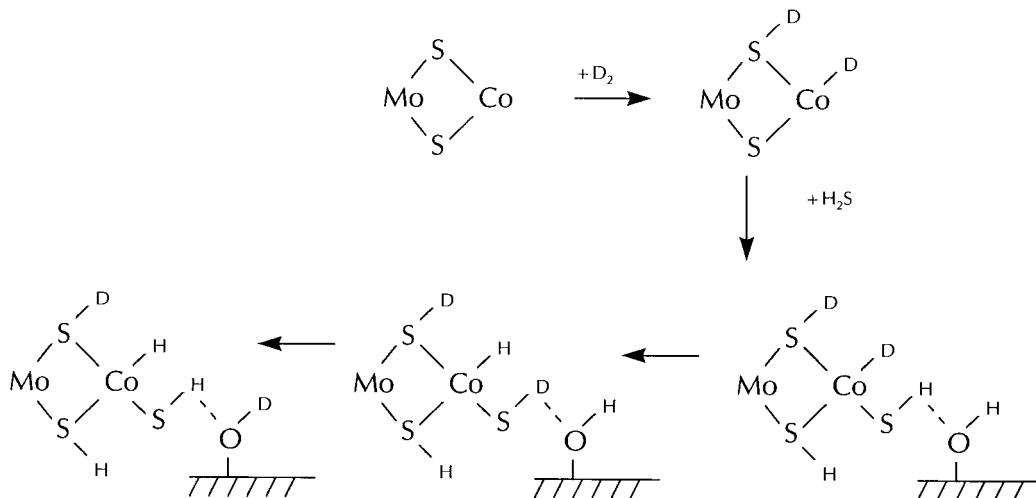

FIG. 8. Schematic representation of catalytic H_2S–D_2 exchange and spillover over a carbon-supported "Co–Mo–S"-type site.

of the CoS_x particles as suggested by the dispersion model. The starting point for this model was the conclusion reached by Vissers *et al.* (6) that the intrinsic thiophene HDS activity per Co atom in Co/C is equivalent to the activity per Co atom in CoMo/C. Our more detailed differential kinetic measurements show that the intrinsic activity per Co atom in CoMo/C(673 K) is substantially higher than the intrinsic activity of Co/C(673 K). Moreover, the remote control model seems inadequate to account for the observed synergy between Co and Mo sulfide. From the present results it is tentatively concluded that the sulfur atoms that bridge between Co^{2+} and Mo^{4+} are important in explaining the synergy between Co and Mo. This is further emphasized by kinetic measurements comparing Mo/C(673 K) and CoMo/C(673 K), which demonstrate that in the former catalyst the activation of $H_2(D_2)$ is rate limiting while in the latter a surface reaction determines the catalytic activity.

It is observed that D atoms, after being adsorbed on the sulfide phase, exchange with H atoms originating from functional groups of the support surface. The rate of this spillover process is much lower that the rate of adsorption and desorption on the sulfide phase but significantly increases by the admixture of H_2S to the gas phase. The results indicate a new pathway for spillover consisting of terminal SH groups in interaction with support functional groups via hydrogen bonding. The lower initial HD formation rate in the presence of H_2S points to competitive adsorption of H_2S and H_2. It is also concluded that H_2 heterolytically dissociates to form a bridging SH group and a metal hydride group while dissociative H_2S adsorption on coordinatively unsaturated sites leads to one bridging SH group and one terminal SH group.

ACKNOWLEDGMENTS

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