Influence of Si/Al Ratio on Catalytic Performance of (Co)Mo/Saponite Catalysts

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In this study the influence of surface acidity of the saponite support on the catalytic performance of sulfided (Co)Mo catalysts is reported. The surface acidity is varied by changing the Si/Al ratio of the tetrahedral layers. Since in many hydrocracking operations hydrodesulfurization also is important two model reactions were employed: hydrocracking of n-decane and HDS of thiophene. Athough the process conditions of these model tests do not resemble commercial operation, the results help to gain a better insight in the effect of a varying Si/Al ratio of the support on which, combined with their acidic properties, makes clays an interesting alternative next to zeolites.

Several studies report on the use of smectite clays in hydrocracking or hydrotreating applications. Kloprogge et al. (12), Sharma et al. (13), and Sychev et al. (14, 15) reported on the use of pillared montmorillonites in the hydrodesulfurization of thiophene. Noble metal catalysts on clay supports displayed a promising performance in hydroisomerization and hydrocracking of model compounds such as n-hexane or n-decane (16–19). Further, tests with gas oil feedstocks were reported by several authors including Occult et al. (20), Monnier et al. (21), and Min (22).

In most of the above-mentioned studies natural clays or clays synthesized under hydrothermal conditions were used. Recently, our group reported on a novel route of synthesis under nonhydrothermal conditions of a class of 2:1 trioctahedral clays called saponites (23). Saponites are layered silicates that are built from octahedral and tetrahedral sheets. The tetrahedral sheets consist of a hexagonal network of primarily (SiO₄)⁴⁻ tetrahedra that are interlinked by sharing all three oxygen corners. Substitution of Si by Al creates Brønsted acid sites similar to zeolites. The octahedral layer is sandwiched between the tetrahedral layers and consists of divalent cations octahedrally coordinated by the apical oxygens of the tetrahedral layer and extra hydroxyl groups. In a former study we explored the use of saponites as supports in hydrosprocessing catalysts (24). It was found that the lattice of Co, Ni, and Zn saponites collapses on exposure to H₂S due to sulfidation of the octahedral layer. Clays containing Mg ions in the octahedral layer are not liable to sulfidation.

In this work of primarily (SiO₄)⁴⁻ tetrahedra that are interlinked

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the catalytic properties. As already well known with zeolite catalysts (25) it will be demonstrated that in hydrocracking the balance between the number of hydrogenation and acid sites has a pronounced effect on the product selectivity. Additionally, in both thiophene HDS and n-decane hydrocracking the activity is affected by the Si/Al ratio. With hydrocracking an almost linear relationship is found between the number of Brønsted acid sites and the conversion of n-decane.

**METHODS**

**Preparation**

Saponites with Mg as the octahedral ion and with varying Si/Al ratios were synthesized at atmospheric pressure as described by Vogels et al. (23). Si/Al gels were prepared from an aqueous solution containing the required amounts of sodium silicate (Merck p.a., 27 wt% SiO₂) and Al(NO₃)₃·9H₂O and aged at room temperature for 1 h. The gels were diluted with demineralized water and the required amounts of urea and Mg(NO₃)₂·6H₂O were added. After synthesis at 363 K for 24 h the saponites were washed with water and ion-exchanged with a 1 M NH₄NO₃ solution. The exchanged samples were dried at 393 K and calcined in air at 723 K.

Characterization with EXAFS

A full optimization of the fits was performed by allowing all parameters of all contributions to vary. Coordination numbers were corrected for the difference in absorber–backscatterer distance between reference compound and unknown assuming an electron mean free path of 5 Å (31). The XDAP data analysis software program was used (32).

**TGA–TPD of Adsorbed n-Propylamine**

TGA and TPD measurements were performed simultaneously using a Perkin Elmer TGS-2 microbalance connected to a Fison Instruments quadrupole mass spectrometer. A sorption was carried out by equilibrating the clay products with n-propylamine vapor at room temperature for 24 h. A weighed amount of sample between 8 and 10 mg was placed in the microbalance and exposed to a 60 ml/min flow of N₂/Ar (10/50). A fter 30 min the temperature was raised from room temperature to 1173 K with a linear heating rate of 10 K/min.

**Catalytic Testing**

Catalytic experiments were performed using an automated microflow apparatus. For each experiment 0.25-1.0 ml of catalyst precursor (sieve fraction 150–425 μm) was placed in a quartz lab reactor (8 mm Ø). Prior to the HDS measurements the catalyst was sulfided in a 100 ml/min flow of H₂S/H₂/Ar (10/40/50) while the temperature was linearly raised from 298 to 673 K (5 K/min) and kept at this temperature for 30 min. Then the flow was switched to 50 ml/min of 2.4 vol% thiophene in H₂/Ar (45/50) at atmospheric pressure. A nalysis of the reactor effluent was done using a gas chromatograph equipped with a Chrompack CP-Sil-5 CB column and a FID. The conversion after 2 min on stream was measured and used to calculate a pseudo-first reaction rate constant (k) according to the relation (33)

\[
k = \frac{1}{\tau \rho} \ln \frac{1}{1 - x},
\]

[1]
in which \( \tau \) is contact time (s), \( \rho \) packing density (kg/dm\(^3\)), and \( x \) conversion. In order to calculate a meaningful rate constant in a second series of experiments the conversion was kept below 90\% by changing the space velocity with the different samples. To prevent slip, the weighed amount of catalyst was diluted with quartz powder (Merck p.a., sieve fraction 200–800 \( \mu \)m) to a total volume of 1.0 ml. It was checked that the choice of taking the conversion at 2 min on stream led to reproducible results.

In order to study deactivation, one of the catalysts was given an oxidative treatment after 6 h HDS at 673 K. The catalyst was heated in O\( _2 \)/Ar (10/90, 100 ml/min) with a rate of 5 K/min from RT to 773 K. After cooling down the sample was again sulfided and exposed to thiophene at 673 K.

The catalytic performance in hydrocracking was tested in the conversion of \( n \)-decane at atmospheric pressure. After sulfidation at 673 K the flow was switched to 50 ml/min of 2.7 vol\% \( n \)-decane in H\( _2 \)/H\(_2\)S/Ar (44.5/0.5/5). The feed contained 1000 ppm H\(_2\)S to ensure that the catalyst stayed in its sulfided state. The conversion was measured during 12 h on stream at 673 K and a pseudo-first-order reaction rate constant was calculated according Eq. [1] after 2 min on stream. The selectivity of the catalysts at 673 K was studied at an intended conversion of 40\% (at 2 min on stream) accomplished by changing the contact time. In other experiments the catalysts were cooled down to 423 K after sulfidation and the conversion curve was measured at every 15 K at temperatures between 423 and 673 K.

**RESULTS**

**Characterization**

The sulfided Co and CoMo catalysts were characterized with EXAFS. Figure 1A shows the \( k^3 \) weighted Fourier

![Figure 1](image.png)
together with that of crystalline MoS₂. The second shell obtained at the Mo–K edge of the sulfided CoMo catalysts is present at 3.54 Å (28). As shown in Fig. 1A the saponite sample with Si/Al ratios of 6 and 26. For reasons of comparison the graph also contains the Fourier transform of crystalline Co₉S₈. In Co₉S₈ the peak between 1 and 3 Å consists of both five sulfur neighbors at 2.21 Å and three Co atoms at 2.51 Å. A second Co–Co contribution of three Co neighbors is present at 3.54 Å (28). As shown in Fig. 1A the amplitude of the Fourier transform of the catalyst samples, notably at the right-hand side (Co–Co), was reduced compared to the bulk sulfide. This is partly due to a decrease of the Co–Co contribution at 2.51 Å (Table 1). The low value of 1.0 of the Co–Co coordination number indicates a highly dispersed cobalt sulfide species in accordance with the almost absence of a second peak in the Fourier transform between 3 and 4 Å. When it is assumed that no bulk sulfide had been formed the average metal sulfide particles contain about 2 Co atoms. The low number of sulfur neighbors, between three and four, suggests that at least part of the Co atoms remains coordinatively unsaturated. It was not possible to incorporate a Co–O contribution in the fit. The quality of the fits is demonstrated in Fig. 1B, which presents the Fourier transform of measured data of the saponite sample with Si/Al l = 6 together with the best fit.

In Fig. 1C the Fourier transforms are shown of the data obtained at the Mo–K edge of the sulfided CoMo catalysts together with that of crystalline MoS₂. The second shell peak between 2.5 and 3.2 Å is due to Mo backscatterers at 3.16 Å and its amplitude is a direct indication of the MoS₂ dispersion (34). The low Mo–O coordination number of about 2 (Table 1) points to molybdenum sulfide slabs containing on average about three or four molybdenum atoms per particle. According to a simple hexagonal model, as recently reported by Shido and Prins, neglect of distortions at the edges of small MoS₂ slabs can lead to an underestimating of the particle size (35). In analogy with an earlier study on highly dispersed MoS₂/alumina catalysts (34), it was tried to include a Mo–O contribution at 2.0 Å in the fit. Although the quality of the fit improved, the Mo–O contribution was statistically not significant. Data analysis did reveal a second Mo–O contribution at 2.7 Å. The latter was also found in a former study on the sulfidation of MoO₃ catalysts supported on alumina and was ascribed to the presence of molybdenum sulfide dimers (36).

**Hydrodesulfurization of Thiophene**

Figure 2A shows the conversion of thiophene over the Co catalysts during 6 h on stream at 673 K measured at a gas space velocity of 3000 h⁻¹. The initial activity slightly increased with decreasing Si/Al ratios. Except for the weakly acidic stevensite all catalysts suffered from deactivation and reached similar levels of conversion (60–70%) after 6 h of reaction. After an oxidative treatment the conversion could be restored to near its initial value, pointing to deactivation due to oligomerization and/or coke formation over the acid sites. Similar observations were made with the CoMo catalysts.

Figure 2B presents the rate constant $k_{HDS}$ after 2 min on stream of the Co and CoMo catalysts versus the number of acid sites determined with TPD–TGA of n-propylamine adsorbed on the unloaded supports. Note that to calculate the first-order rate constant $k_{HDS}$ using Eq. [1], a second series of experiments was performed in which the conversion was lowered by measuring with a higher space velocity (12,000 h⁻¹). The amount of n-propylamine desorbing from saponites between 615 and 725 K can be used to quantify the number of catalytically active Brønsted acid sites as demonstrated by Gorte and coworkers (37, 38). The application of this technique to the determination of the surface acidity of synthetic saponites is discussed elsewhere (39). As Fig. 2B displays with the Co catalysts a small beneficial effect of the support acidity on the HDS activity was observed. The saponites all displayed a significant higher activity than the stevensite ($k_{HDS}$ increases from 2.3 dm³/kg·s for the stevensite to 3.5 dm³/kg·s for the saponite with Si/Al l = 6; estimated accuracy in k ± 7%). Remarkably, with the CoMo catalysts just the opposite behavior was observed and the activity decreased with an increasing number of acid sites.

The product selectivity was also affected by the presence of acid sites. Besides such usual HDS products as cis- and trans-...
trans-butene and butane, iso-butane and <C3, C3, and C5 products were also observed. These latter compounds can be formed through acid catalyzed reactions. Due to their similar retention times the GC peaks of 1-butene and iso-butene could not be separated and the individual presence of the two compounds could not be determined. As demonstrated in Figs. 2c and 2d the selectivity after 2 min time on stream toward iso-butane and <C3, C3, and C5, measured at conversions between 90 and 100%, was on the whole found to increase with increasing support acidity. However, since the conversion level was above 90%, it is not permitted to draw any conclusions from this. To study whether the observed iso-butane was produced by hydrogenation of iso-butene or by isomerization of butane an experiment was performed under exactly the same conditions with a feed of 1% butane in Ar. No conversion was observed, indicating that iso-butane in the HDS of thiophene is produced by hydrogenation of iso-butene.

**Hydrocracking of n-Decane**

The performance in the hydrocracking of n-decane of the clay catalysts was found to be related to both the Si/Al ratio of the support and the hydrogenation capacity of the metal sulfide. Figure 3 represents the first-order rate constant $k_{HYC}$ (calculated according to Eq. [1]) versus the number of acid sites determined with TPD-TGA of n-propylamine. The activity of the catalysts generally increased with an increasing degree of substitution of Si by Al. Remarkably, the stevensite samples, with no substitution of Si by Al, displayed a considerable activity. The CoMo catalysts were more active than the Co catalysts with comparable Si/Al ratios. As with thiophene HDS the catalysts suffered from deactivation and reached similar levels of conversion after 12 h on stream. The impregnated Co catalysts all deactivated to conversions of about 20% (stevensite at around 10%). The CoMo samples reached conversion levels of
FIG. 3. First-order reaction rate constant for \( n \)-decane hydrocracking \( \text{HYC} \) at 673 K of the Co (squares) and CoMo catalysts (open circles) versus number of acid sites determined by TPD–TGA of \( n \)-propylamine.

about 30% (stevensite 20%). The space velocity in these experiments was 3000 h\(^{-1}\).

To compare the selectivity of the different catalysts the effect of the conversion and the temperature on the selectivity was investigated. Figures 4A and 4B compare the selectivity of the CoMo catalyst with a Si/Al ratio of 6 at two different levels of conversion (45 and 90%). With rising conversion the selectivity toward \( C_3 \) hydrocarbons increased. However, although the conversion differs by a factor 2 the selectivity only rises about 2.5%. The effect of the conversion on the selectivity toward unsaturated products is more pronounced. A sharp decrease is observed with increasing conversion or longer contact times. The effect of the temperature on the selectivity is demonstrated in Figs. 4B and 5C for the same sample after 12 h of stabilization at 673 K. Decreasing the reaction temperature from 673 to 633 K changes the selectivity pattern drastically. The selectivity toward \( C_3 \) decreases from 31 to 22%, balanced by a higher selectivity toward the heavier hydrocarbons (\( >C_3 \)). Also less unsaturated compounds are observed at 633 K.

The influence of the support acidity on the selectivity is shown in Fig. 5 with the CoMo catalysts. The selectivity toward \( C_3 \) gradually drops from 37 to 22% on changing the Si/Al ratio from 6 to 39. As was demonstrated above, these changes are not likely to be caused by the different levels of conversion (46 vs 30%), since such a change in conversion only causes variations in selectivity of 2–3%. The selectivity pattern of the stevensite sample is quite different from that of the saponite samples; it has a much more even distribution over the number of carbon atoms and a reasonable production of isomerized \( C_{10} \) compounds. With the Co saponites no changes in selectivity were observed as a function of the Si/Al ratio. The Co saponite samples all exhibited a product selectivity similar to that of the CoMo sample with a Si/Al ratio of 6 (Fig. 5A). The stevensite Co

FIG. 4. Selectivity towards \( C_1-\text{C}10 \) hydrocarbons of CoMo/saponite Si/Al = 6 in \( n \)-decane conversion after 2 min on stream at conversions of (A) 45% and (B) 90%. Selectivity of CoMo/saponite Si/Al = 6 in \( n \)-decane conversion after stabilization at 673 K (C) at 633 K (11% conversion) and (D) at 673 K (12% conversion).
FIG. 5. Selectivity toward C1–C10 hydrocarbons of the CoMo clays in n-decane conversion after 2 min on stream; Si/Al ratios of (A) 6 (46% conversion), (B) 12 (38%), (C) 26 (35%), (D) 39 (30%), and (E) stevensite (30%).

catalyst revealed a product selectivity resembling that of the CoMo stevensite.

Finally, the activity of the unloaded saponites was tested. The activity increased with increasing support acidity. The first-order rate constant \( k_{\text{HYC}} \) of the saponite with a Si/Al ratio 6 amounted to 0.2 dm\(^3\)/kg · s, considerably lower than that of the impregnated samples. It was observed that removal of H\(_2\) from the feed (50 ml Ar instead) had no effect on the conversion. This indicates that over the unloaded supports cracking takes place instead of hydrocracking.

Temperature Programmed Hydrocracking

Surprisingly, when the activity was measured as a function of decreasing reaction temperature a maximum in the conversion was found in the temperature region around 523 K. In order to study this phenomenon with catalysts that had not suffered from deactivation, conversion curves were recorded at ascending temperatures between 393 and 673 K with freshly sulfided samples. As displayed in Fig. 6A for the CoMo catalysts the conversion reached an optimum at about 523 K, the maximum value rising with an increasing
regeneration, indicating the occurrence of coking. Hence, it is reasonably assumed that a similar mechanism of deactivation takes in the hydrocracking of n-decane at elevated temperatures.

Since the stevensite sample did not show any activity at low temperatures the maxima in the conversion curves must be related to the presence of the acid sites on the saponite supports. Since it is well known that dehydroxylation of the support can lead to the loss of Brønsted sites the conversion was also measured at descending temperatures to study whether the conversion drop between 523 and 573 K was reversible. To ensure that the feed contained no water that could redsorb during cooling down, the gas stream was dried over Sicapent (Merck). As shown in Fig. 6B the maximum in the conversion curve was almost completely restored on cooling down, indicating that dehydroxylation was not likely to cause the optimum in the conversion. In contrast to this, it turned out that omission of H₂S from the feed strongly affected the course of the activity (Fig. 6C). At ascending temperatures the maximum conversion attained a value of only 14%, while at descending temperatures the activity reached a maximum of only 5% conversion. The observed activity between 423 and 573 K is obviously brought about by a combination of the acid sites on the support and the presence of H₂S in the feed. Finally, when the sulfided catalyst was exposed to water vapor before reaction the activity in the region of 523 K was completely lost, indicating poisoning of the acid sites by water adsorption.

**DISCUSSION**

Dispersion and Location of Metal Sulfide Particles

In the Co and CoMo catalysts a high dispersion of both the supported cobalt sulfide and the molybdenum sulfide phase independent of the Si/Al ratio of the support was found. Unfortunately, the cobalt sulfide phase in the CoMo catalyst was not characterized with EXAFS at the time and no data are available on its dispersion.

It is known that Mo hydrolyzes in aqueous solutions to form (Mo₂O₇)⁶⁻ and (MoO₄)²⁻ ions while Co occurs as CoOH⁺ or Co₂O₃H³⁺ ions in aqueous solutions (40). Apparently, since both the cobalt sulfide and the molybdenum sulfide dispersion are quite high, a good interaction exists between the surface of the saponite sheets and both positively and negatively charged ions. This dual behavior might be explained by the existence of a positive electrical double layer on the edges of the clay particles and a negative double layer on the faces (top and bottom planes) of the clay platelets (41). In this model the positively charged cobalt ions are thus assumed to adsorb preferentially on the faces of the clay platelets while the negatively charged molybdenum ions interact with the positively charged edges of the clay platelets.

**FIG. 6.** (A) Conversion of n-decane (space velocity 3000 h⁻¹) of the various sulfided CoMo catalysts measured at ascending temperatures. (B) Conversion of n-decane (space velocity 3000 h⁻¹) measured at ascending and descending temperatures of the CoMo/saponite Si/Al = 12 with H₂S in the feed. (C) As Fig. 7b without H₂S in the feed.

The degree of substitution of Si by Al. Beyond 573 K the conversion increased again, but did not follow a first-order conversion curve. This concave shape of the curves is ascribed to deactivation of the catalysts at higher temperatures due to coke formation. With the HDS experiments it was observed that the catalyst activity could be restored by an oxidative regeneration, indicating the occurrence of coking. Hence, it is reasonably assumed that a similar mechanism of deactivation takes in the hydrocracking of n-decane at elevated temperatures.

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HDSS Activity and Product Selectivity

The thiophene HDSS test results show that the initial HDSS activity of the Co catalysts considerably increases when saponite is used as support instead of stevensite. Since the dispersion of the cobalt sulfide phase is similar this must be related to the acidic nature of the saponite. A positive correlation between the acidity of the support and the HDSS activity was also reported by Welters et al. (42) in a study of the HDSS performance of metal sulfides supported on H(x)NaY, ZSM-5, and H-U SY zeolites. Several possibilities were discussed as an enhanced adsorption of thiophene in the zeolite pores, acceleration of the rate determining step through involvement of protons, and formation of a higher number of SH groups on the metal sulfide phase. Although we cannot present any evidence another possibility is that the acidity of the support affects the catalytic properties of the supported metal sulfide particles through small changes of the electronic structure of the metal sulfides.

Remarkably, the initial activity of the CoMo catalysts clearly decreases with increasing support acidity, in contrast with the work of Welters et al. (42) and the findings with the Co catalysts. In the CoMo catalyst the promoter atoms can either be present on the faces of the clay platelets or be associated with Mo in the very active “Co–Mo–S” phase. Decreasing the Si/Al ratio of the support will increase the negative charge on the clay platelets, enhancing the adsorption of the positively charged Co ions on the clay faces away from the Mo. Since Co–Mo–S is known to be more active than the sum of separate Mo and Co sulfides, this might explain the decrease in activity with a higher support acidity. Interestingly, in the hydrocracking experiments the opposite behavior is observed, i.e., the activity of the CoMo catalysts increases with increasing support acidity. This can be ascribed to either an increased activity of the hydrogenation sites (assumed that for hydrogenation the effect of synergy between Co and Mo in a Co–Mo–S structure is low) or to a larger number of acid sites. The latter explanation is supported by the linear relationship between the number of acid sites and the rate of the hydrocracking reaction (vide infra).

The detection of <C3, C3, and C5 as reaction products is in accordance with the results of Hozvicka et al. (43) in which the authors demonstrated that Bønsted acid sites are the active sites in the skeletal isomerization of n-butene. n-Butene formed in the HDS of thiophene is isomerized to iso-butene over the acid sites of the support. Subsequently, the iso-butene is hydrogenated to iso-butane. The formation of <C3, C3, and C5 proceeds through dimerization of C4 followed by cracking (44). The dimerization of C4 also gives rise to oligomerization, resulting in coking of the catalysts and the observed initial deactivation.

Balance between Hydrogenation and Acid Sites

The activity in the hydrocracking of n-decane rises with decreasing Si/Al ratios. With the CoMo samples an almost linear relationship is observed between the number of acid sites and the pseudo-first-order rate constant $k_{H2C}$. In the classical mechanism of bifunctional hydrocracking dehydrogenation of n-decane takes place over the hydrogenation sites followed by one or more skeletal rearrangements over the acid sites and subsequent hydrogenation of the product alkenes by the sulfide sites (45, 46). Provided that the (de)hydrogenation capacity is sufficiently high the rearrangements will be the rate limiting step (47). A positive correlation between the acidity of the support and the HDS activity was also reported by Welters et al. (42) in a study of the HDSS performance of metal sulfides supported on H(x)NaY, ZSM-5, and H-U SY zeolites. Several possibilities were discussed as an enhanced adsorption of thiophene in the zeolite pores, acceleration of the rate determining step through involvement of protons, and formation of a higher number of SH groups on the metal sulfide phase. Although we cannot present any evidence another possibility is that the acidity of the support affects the catalytic properties of the supported metal sulfide particles through small changes of the electronic structure of the metal sulfides.

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Generation of Acidity by H2S

The observed maximum at low temperatures in the hydrocracking activity seems to be due to a combination of Si–OH–Al sites with H2S. The results clearly demonstrate a relation between activity and Si/Al ratio and the influence of the partial pressure of H2S. Additionally, the involvement of Si–OH–Al sites is also suggested by the loss of activity after prior exposure to water vapor. Water can act as a poison by irreversible adsorption on the acid sites (at least at low temperature).

The formation of Brønsted acid sites by reversible adsorption of H2S has previously been reported by Sugioka et al. (51) for various alkali metal zeolites. These authors proposed that the generation of these acid sites is caused by nondissociative adsorption of H2S as H–S–H groups exhibiting Brønsted acidity. Alternatively, dissociative adsorption of H2S was proposed over Na+ ions, leading to excess protons forming new acidic –OH groups. (52). A (reversible) adsorption of H2S creating Brønsted activity may also occur in saponites. However, that the created acid sites are stronger than the original acid sites seems not logical and cannot be explained. Interestingly, in a recent paper by Stumbo et al. (53) on physical mixtures of CoMo/SiO2 and silica–aluminas, the creation of acid Brønsted sites was proposed to occur by migration of spillover species from the CoMo catalyst to the silica–aluminas. This process was accelerated in the presence of both H2O and H2S. Such a migration of spillover species might also take place in the saponite catalysts.

Altogether, the current experimental results do not allow to find a satisfying explanation for the hydrocracking activity at low temperature. However, the results are intriguing and indicate the complexity of hydrocracking induced by the presence of a variety of gaseous and solid components.

CONCLUSIONS

In this study the relation between the performance of clay supported (Co)Mo sulfides and the acidity of the support, varied through means of the Si/Al ratio, was investigated. In the hydrodesulfurization of thiophene an increasing number of Brønsted acid sites affects both the activity and selectivity. With Co catalyst a small increase in the initial activity is observed when Si is substituted for Al. However, with CoMo catalysts a decrease of the initial HDS activity with decreasing Si/Al ratios is observed. This observation is ascribed to a lower relative amount of Co–Mo–S due to preferred adsorption of Co ions on the faces of the saponite platelets and adsorption of Mo on their edges. The acid sites on the support are able to isomerize n-butene into isobutene with high yields. Further, a clear relationship was found between the number of acid sites and the selectivity toward cracking products formed through acid catalyzed reactions.

In the hydrocracking of n-decane the activity of the catalysts rises with an increasing degree of substitution of Si by Al in the support. With CoMo impregnated samples a linear relationship is observed between the number of Brønsted sites and the first-order reaction rate constant. A ll cobalt sulfide catalysts and the CoMo catalysts with low Si/Al ratios are deficient in their hydrogenation capacity, leading to a rather high selectivity toward secondary cracking products. Further, the ratio between the number of hydrogenation sites and the number (and possibly strength) of acid sites determines the degree of hydroisomerization versus hydrocracking.

Finally, it was observed that interaction of H2S with the support leads to extra activity at low temperature in the hydrocracking of n-decane. The positive relation between the degree of Si for Al substitution and the "low-temperature" activity points to the involvement of the Si–OH–Al I groups on the surface of the saponite support.

REFERENCES