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Catalytic activity of nickel sulfide catalysts supported on Al-pillared montmorillonite for thiophene hydrodesulfurization

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Abstract

Al-pillared clays, prepared by exchange with partly hydrolyzed aluminium nitrate solutions, dried in air or freeze-dried, and calcined, were used as supports for nickel sulfide catalysts. The catalysts were tested on their hydrodesulfurization (HDS) activity for thiophene. The catalysts show a high thiophene HDS activity. It appears that details in the preparation and calcination of the pillared clays have a strong influence on the catalytic activity.

Keywords: aluminium-pillared montmorillonite; nickel sulfide; thiophene hydrodesulphurization

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INTRODUCTION

Pillared clays are considered to be interesting two-dimensional, shape-selective, molecular sieves of a larger pore size range than zeolites. In 1955 Barrer and MacLeod [1] developed the idea of pillaring montmorillonite with organic compounds. However, these organic pillars decompose at relatively low temperatures, resulting in the collapse of the pillared clay structure. Utilization of inorganic polyoxocations, mainly Al [2] and Zr [3,4] as pillaring agents dealt with the problem of the thermal stability. On calcination the polyoxocations react to immobile oxide pillars resulting in a permanent microporosity in the clay interlayers.

The Al polyoxocation, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al13), formed during forced hydrolysis of Al^{3+} under specific conditions [5,6], has a Keggin-type structure, consisting of a central fourfold coordinated Al surrounded by twelve sixfold coordinated Al [7-9]. The existence of Al13 in solution was proven by ^{27}Al nuclear magnetic resonance (NMR) (see references in ref. 10) and small-angle X-ray scattering [11].

Al-pillared clays exhibit a reduction of the cation exchange capacity (CEC) [12], an increase in basal spacing, surface area, thermal stability [13,14], and both Brønsted and Lewis acidity, the last becoming dominant upon calcination [14,15]. Only few data have thus far been reported on metal sulfide catalysts supported on pillared clays. Warburton [16] used clays pillared by Fe-sulfide for the high-pressure demetallization of heavy crude oil. Ocelli and Rennard [17] applied pillared bentonite as a support for Ni-Mo catalysts for the hydrogenation-hydrocracking of vacuum gas oil feedstocks. In both cases the catalysts exhibited interesting catalytic properties.

Studies on nickel sulfide catalysts have indicated that during the preparation of the catalyst, supports such as Al_2O_3 , interact significantly more strongly with the Ni^{2+} cations than carbon supports, which only exhibit a weak interaction. Pillared clays provide an interesting intermediate case. Whereas the alumina pillars will react with the Ni^{2+} cations, the clay sheets are probably less reactive. The catalytic properties of the pillared clay supported nickel sulfide phase are probably comparable to the zeolite supported ones. Welters et al. [18] have recently demonstrated that sulfidation of NiNaY zeolites produces highly active desulfurization catalysts. Hence, sulfidation of nickel catalysts supported on pillared clays may, depending on whether the main part of the nickel phase will interact with the alumina pillars or with the clay sheets, be able to produce highly active metal sulfide catalysts.

This paper compares the activity for thiophene hydrodesulfurisation (HDS) at atmospheric pressure of nickel sulfide catalysts supported on Al13-pillared montmorillonite to alumina and carbon supports.

EXPERIMENTAL

Starting clay

The Na-montmorillonite SWy-1 from the Newcastle Formation, Crook County, Wyoming, was obtained from the Source Clay Repository of the Clay Mineral Society. Small amounts of quartz, calcite, and K-feldspar are present [19]. Therefore, chemical analyses can only yield an approximate structural formula of $(K_{0.01}Ca_{0.04}Na_{0.30})(Al_{1.54}Mg_{0.26}Fe_{0.20})(Si_{3.93}Al_{0.07})O_{10} \cdot nH_2O$ and a CEC of 85 meq/100 g clay [20].

The fraction smaller than 2 μm was obtained by gravity sedimentation and decantation, followed by washing four times with 1 M NaCl solution and removing the excess electrolyte by washing five times with deionized water.

Pillaring agent

Aluminum tridecamer solutions were prepared by injection at a rate of 0.015 ml/s of 0.2 M NaOH (Merck) solution using a Gilson pump (capillary diameter of 0.5 mm) below the surface of an 0.5 M $Al(NO_3)_3$ (Merck) solution, which was vigorously stirred, until the desired OH/Al molar ratio of 2.4 was reached [5]. These solutions contain approximately 70% Al13 polymer [5].

Pillaring process and characterization of the pillared clays

The Al13 solutions were rapidly added under vigorous stirring to specified volumes of clay slurries, containing 20 g of solid/l, to attain ratios of 5.5 and 20 meq Al/g clay. After 12 h exchange the pillared clays were washed five times with deionized water, followed by air- or freeze-drying and calcination at temperatures between 473 and 973 K. The pillared clays were characterized by means of X-ray powder diffraction, using a Philips PW 1050/25 diffractometer (Cu $K\alpha$), to measure the basal spacing, and nitrogen adsorption to obtain the BET surface area using a ASAP 2400 surface area and pore volume analyzer (Micromeritics Instrument Corporation).

Catalyst preparation

The catalysts were prepared by pore volume impregnation of the pillared clays with appropriate solutions of nickel chloride ($NiCl_2 \cdot 6H_2O$, Merck p.a.). The concentration of the metal salt solution was adjusted so as to obtain a nickel loading of 4.0 wt.-% Ni per gram of catalyst. Alumina (Ketjen 001-1.5E) and carbon (Norit RX3-Extra) supported nickel sulfide catalysts were prepared according to the same procedure. All catalysts were dried in air at 383 K for 16 h.

Activity measurements

Catalyst samples (200 mg, 0.125 to 0.425 mm particle size) were presulfided in situ in a H₂S/H₂ flow (10 mol-% H₂S, 60 ml/min) using the following temperature program: a 6 K min⁻¹ increase from 293 K to 673 K and keeping the catalyst for 2 h at 673 K. Following the sulfidation the gas flow was switched to the reaction mixture: a hydrogen flow containing 4.0 mol-% thiophene (Janssen Chimica). The reaction conditions were: flow-rate 50 ml min⁻¹, reaction temperature 673 K, and pressure 1 bar. The thiophene conversion was measured at different time intervals by on-line gas chromatography. First order rate constants for thiophene HDS (k_{HDS}) were calculated as described elsewhere [21].

RESULTS AND DISCUSSION

Table 1 summarizes the basic characteristics of the pillared montmorillonites. Upon pillaring the basal spacings of the montmorillonites increase from 12.5 Å to 18.8 Å. Upon calcination up to 873 K a decrease to 16.9 Å is observed. The calcined samples show a considerable drop in BET surface area and micropore (pores diameter <20 Å) volume fraction. The freeze-dried samples exhibit a BET surface area increasing with calcination at temperatures up to 673 K and a nearly constant micropore volume fraction, followed by a strongly diminishing surface area at 873 K. An extensive characterization of these pillared montmorillonites is given by Booij [22].

The results of the activity measurements are represented in the Figs. 1 to 3. The reaction rate constant for the hydrodesulfurization of thiophene is plotted

TABLE 1

Basal spacings (Å), BET surface areas (m²/g), and micropore (diameter <20 Å) volume as percentage of total pore volume of the montmorillonite SWy-1 and the pillared analogues

Sample	meq Al/g	Drying	$T_{\text{calcination}}$ (K)	d_{001} (Å)	BET (m ² /g)	Micropore vol. (%)
SWy-1	—	—	298	12.5 ± 0.1	25.6 ± 0.1	2.9
PILC11	5.5	air	298	18.8 ± 0.3	348.8 ± 2.3	77.2
PILC6	5.5	air	623	17.6 ± 0.3	269.0 ± 1.6	54.3
PILC7	5.5	air	773	17.0 ± 0.3	150.2 ± 0.4	37.2
PILC17	5.5	freeze	473	17.0 ± 0.3	226.4 ± 1.2	43.9
PILC19	5.5	freeze	573	17.0 ± 0.3	270.4 ± 1.6	54.2
PILC20	5.5	freeze	673	17.0 ± 0.3	317.6 ± 1.7	53.0
PILC22	5.5	freeze	873	16.9 ± 0.3	189.5 ± 0.6	50.0
PILC26	20.0	freeze	623	17.4 ± 0.3	280.6 ± 1.7	62.4
PILC27	20.0	freeze	773	16.7 ± 0.3	n.d.	n.d.

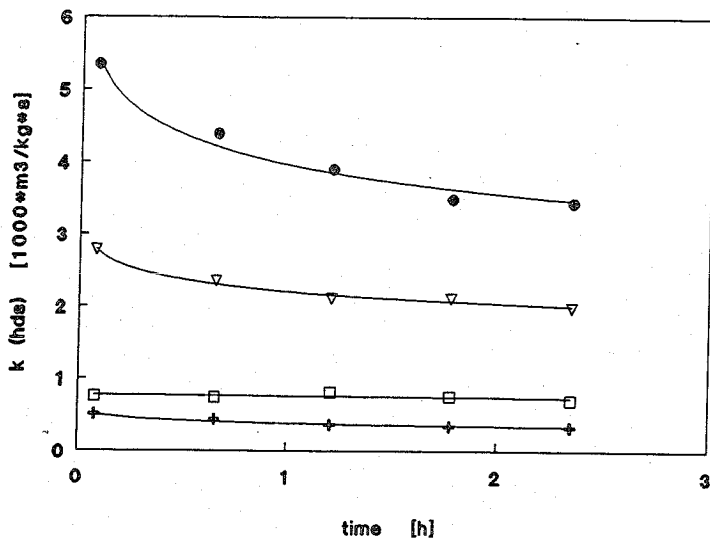


Fig. 1. Reaction rate constant for thiophene HDS as a function of time-on-stream for various supports: (\square) 4 wt.-% Ni on Al_2O_3 , (∇) 4 wt.-% Ni on C, ($+$) 4 wt.-% Ni on SWy-1, (\bullet) 4 wt.-% Ni on PILC26.

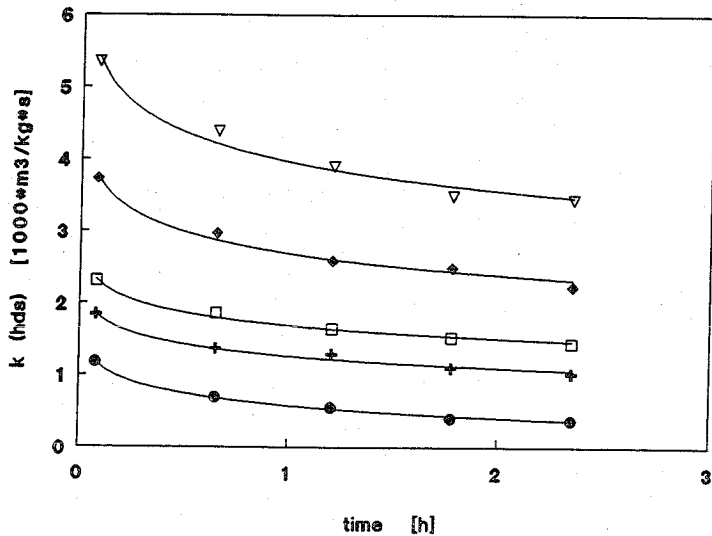


Fig. 2. Reaction rate constant for thiophene HDS as a function of time-on-stream for: ($+$) 4 wt.-% Ni on PILC17, (\bullet) 4 wt.-% Ni on PILC19, (\square) 4 wt.-% Ni on PILC20, (∇) 4 wt.-% Ni on PILC22.

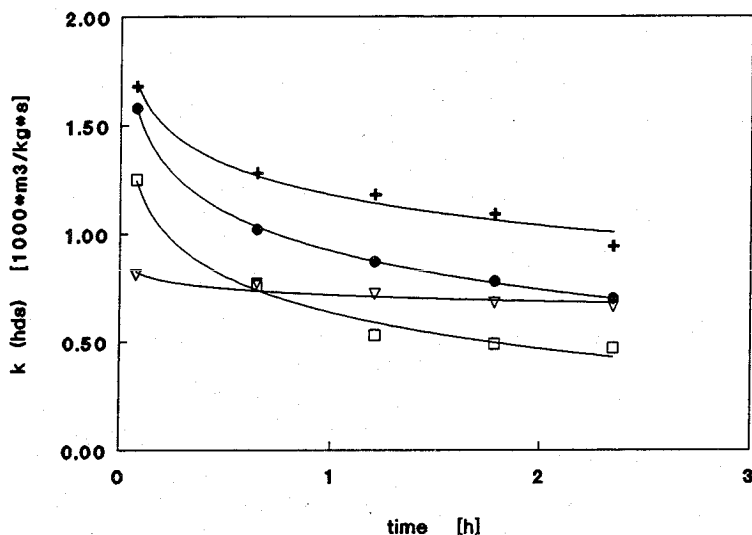


Fig. 3. Reaction rate constant for thiophene HDS as a function of time-on-stream for: (+) 4 wt.-% Ni on PILC6, (●) 4 wt.-% Ni on PILC7, (□) 4 wt.-% Ni on PILC11, (▽) 4 wt.-% Ni on PILC26, (◆) 4 wt.-% Ni on PILC27.

as a function of the time-on-stream for several catalysts. In Fig. 1 two catalysts not based on clay are compared with a non-pillared and a pillared montmorillonite (SWy-1 and PILC26) catalyst. The activated carbon-supported catalyst shows a much better HDS activity than the alumina-supported catalyst, as known from literature [21,23–25]. The interaction between the metal ions and the support is much stronger for Al_2O_3 than for C, resulting in a lower activity for the alumina-supported catalysts.

The montmorillonite-supported sample shows an even lower activity than the alumina-supported sample. This may be due to a low nickel sulfide dispersion caused by the low surface area and the very low fraction of micropores in the non-pillared sample (Table 1). The HDS activity of the catalysts prepared from pillared clays, however, is strikingly higher than that of the non-pillared clay. As an example the activity of PILC26, which is even higher than that of the carbon-supported catalyst, is given in Fig. 1. The SiO_4 groups in the tetrahedral layer are, like carbon, inert to nickel. Therefore, catalysts supported on pillared clay are expected to have a rather low metal-support interaction causing a sulfidation chemistry more to resemble that of carbon supports [26–28].

The thiophene HDS activity of nickel sulfide catalysts supported on pillared clays prepared by freeze-drying and calcining at different temperatures (Fig. 2), decreases with increasing calcination temperature, except for PILC22. This effect can be explained by several factors, which can all have some influence on the activity of the catalysts. Firstly, the interaction between the support

and the nickel sulfide phase might change with increasing calcination temperature. Raising the calcination temperature increases the dehydration and dehydroxylation of the Al13 pillars that react to oxide pillars resembling γ -Al₂O₃ [29] according to the overall reaction $\text{Al13} \rightarrow 6.5 \gamma\text{-Al}_2\text{O}_3 + 7 \text{H}^+ + 20.5 \text{H}_2\text{O}$. Upon increasing the calcination temperature a stronger metal-support interaction can be expected and, hence, a decreasing activity of the nickel sulfide particles, as indeed is observed.

A second factor which may influence the activity is the dispersion of the active phase. The differences in surface area are probably too small to influence the dispersion of the nickel sulfide in such a way that it can explain the activity differences. Different surface properties, however, can also influence the dispersion. The decreased interaction upon calcination may lower the nickel sulfide dispersion, resulting in a lower HDS activity.

The third factor that may influence the activity of the catalyst is the acidity. Welters (unpublished results) has recently found indications for zeolite supports that changes in acidity can affect the sulfide dispersion. Increasing the calcination temperature will lower the acidity of the clay due to loss of protons released from the pillars. The release of protons may also have some influence on the dispersion and HDS activity of the catalyst, especially the initial activity. The presence of initial acid sites on the clay support and those created during the formation of the oxide pillars is probably responsible for the deactivation due to coke formation. The PILC22 sample, calcined at 873 K, does not show any deactivation because no Brønsted acidity is left after complete dehydration and dehydroxylation of the pillared clay. The same trend of decreasing activity with increasing calcination temperature as for the samples exchanged with 5.5 meq Al/g clay is observed for samples exchanged with 20 meq Al/g clay and for air dried samples (Fig. 3).

Montmorillonites exchanged with 20 meq Al/g clay exhibit a much higher HDS activity than those exchanged with 5.5 meq Al/g clay (Fig. 3). As compared to the 5.5 meq Al/g pillared clays, the 20 meq Al/g samples do not show any significant difference in basal spacing or amount of alumina pillars per gram of clay, and only slightly higher BET surface and average micropore size. The lack of significant differences indicates that zero charged montmorillonite upon saturation with Al13 pillars is established with 5.5 meq Al/g clay, which agrees with the results of Gu and Doner [30]. The only difference observed, accompanying a small increase in absolute pore volume up to calcination at 673 K, is a rise of the micropore volume from approximately 50 to 62% of the total pore volume, suggesting a more homogeneous pillar distribution. Figueras et al. [31] observed an increasing homogeneity of the pillars upon competitive ion exchange of NH₄⁺ and Al13. They argued that diffusion of Al13 with a kinetic radius of about 10 Å [32] is restricted in the interlayer space of smectites. The high selectivity of the clay for Al13 apparently precludes a good distribution, preventing the Al13 polymers from diffusion into the core of the

interlayer. Increasing the amount of Al₁₃ per gram of clay, without altering the Al concentration in solution, seems to decrease the diffusional limitations. The better distribution of pillars between the sheets and the higher micropore volume may also influence the distribution of the nickel species, resulting in a higher dispersion of the nickel sulfide phase.

Also the drying procedure (freeze- or air-drying) of the pillared montmorillonites affects the activity for thiophene HDS. Air-drying of the 5.5 meq Al/g pillared clays leads to catalysts showing slightly higher reaction rates in comparison to freeze-dried 5.5 meq Al/g clays calcined at the same temperatures. The air-dried samples exhibit slightly smaller external surface areas and mesopore volumes in comparison with the freeze-dried samples. The difference may be explained by the aggregation of the montmorillonite platelets in a face-to-face orientation, whereas freeze-dried samples have aggregates mostly formed by three-dimensional edge-to-edge and edge-to-face configuration, like a house of cards [33,34]. These structures are probably retained upon calcination and impregnation with Ni²⁺, causing small differences in the nickel sulfide dispersion leading to the slightly higher HDS activity of the air-dried samples.

Concluding it can be said that pillared clay supported nickel sulfide catalysts are very promising catalysts, with which interestingly high HDS activities can be achieved. Detailed characterization of the pillared clays after impregnation with Ni²⁺ and sulfidation is required to explain the observed differences in catalytic activity for thiophene hydrodesulfurisation.

CONCLUSIONS

It has been demonstrated that montmorillonite can be impregnated with nickel followed by sulfidation to provide catalysts exhibiting comparable and even higher thiophene HDS activities than alumina- and carbon-supported nickel sulfide catalysts. The catalytic activity is shown to increase by raising the amount of Al₁₃ pillars from 5.5 meq Al/g to 20 meq/g, whereas an increase in calcination temperature results in an activity loss. 5.5 meq Al/g is sufficient to saturate the montmorillonite.

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