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Citation for published version (APA):

Sychev, M. V., Beer, de, V. H. J., Santen, van, R. A., Prihod'ko, R. V., & Goncharuk, V. V. (1994). Some aspects of the preparation and catalytic activity of chromia pillared montmorillonite. In A. K. Cheetham (Ed.), *Zeolites and related microporous materials: state of the art 1994 : proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, July 17 - 22, 1994* (pp. 267-274). (Studies in Surface Science and Catalysis; Vol. 84). Elsevier. [https://doi.org/10.1016/S0167-2991\(08\)64123-3](https://doi.org/10.1016/S0167-2991(08)64123-3)

DOI:

[10.1016/S0167-2991\(08\)64123-3](https://doi.org/10.1016/S0167-2991(08)64123-3)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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SOME ASPECTS OF THE PREPARATION AND CATALYTIC ACTIVITY OF CHROMIA PILLARED MONTMORILLONITE

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Chromia pillared montmorillonites with basal spacing 2.4-2.6 nm have been synthesized from Na- and Ca- cationic forms of the mineral and characterized by a variety of methods. In 2-propanol and ethanol decomposition respectively at 413 K and 623 K these materials exhibit dehydration and dehydrogenation properties. The Cr-PILM's activated by in H_2S/H_2 mixture show an interestingly high activity for thiophene HDS and the consecutive hydrogenation of butenes.

1. INTRODUCTION

Pillared clays derived from smectites interlayered with inorganic polymeric cations represent a relatively new class of porous materials. These materials can possibly replace zeolite-containing catalysts for certain reactions [1].

Chromia pillared smectites are of particular interest because the pillaring phase itself is catalytically active. Such catalysts are claimed to possess remarkable activity in cyclohexane dehydrogenation, hydrocracking of n-decane [2,3], toluene disproportionation [1], as well as exhibit dehydrogenation activity for cumene conversion [4].

Most of the early attempts to incorporate oligomeric chromium ions in the galleries of smectites made use of chromium nitrate solution hydrolyzed at room temperature [5]. However, chromia pillared montmorillonite (Cr-PILM) prepared in accordance with this method has a spacing of only 1.68 nm [5]. Therefore, Tzou and Pinnavaia proposed the use of higher temperatures for pillaring reagent formation and for cross-linking of the clay mineral [3]. As a result of this, Cr-PILM's with substantially larger spacing than those of materials formerly obtained were prepared. Recently Cr-PILM was synthesized via in situ hydrolysis of chromium acetate on a clay surface [6]. By means of the above methods (depending on synthesis conditions) microporous Cr-PILM materials with BET surface area ranging from $250 \text{ m}^2\text{g}^{-1}$ to $433 \text{ m}^2\text{g}^{-1}$ and spacing in the range of 2.1-2.7 nm can be obtained [3,6]. However, many relations between preparation parameters and properties of the Cr-PILM are not really clear yet.

The purpose of the present work is preparation of the Cr-PILM from monovalent (Na^+) and divalent (Ca^{2+}) cationic forms of montmorillonite and investigation of the influence of some parameters on the texture of the materials prepared. In addition catalytic properties for alcohol decomposition and thiophene hydrodesulfurization are evaluated.

2. EXPERIMENTAL SECTION

Clay samples. Oglanlinsky montmorillonite (Kazakhstan, CIS) with anhydrous unit cell formula $\text{Na}_{0.54}\text{K}_{0.02}\text{Ca}_{0.09}(\text{Si}_{8.57}\text{Al}_{0.24})(\text{Al}_{1.85}\text{Fe}_{0.11}\text{Mg}_{0.66})\text{O}_{20}(\text{OH})_4$ and cationic exchange capacity (CEC) of 85 meq/100 g was chosen as starting material. Sodium- and calcium cationic forms of the mineral used in this study were prepared following the technique described elsewhere, e.g. by Tokarz and Shabtai [7]. A fraction containing particles smaller than $< 2\mu$ collected by sedimentation, was used in a form of aqueous suspension (1 wt.%) for chromia pillared montmorillonite preparation. The preparation method is similar to the method of Tzou [2].

Pillaring reaction. The pillaring reagent containing chromium oligomers was formed by heating a 0.10 M solution of chromium nitrate with Na_2CO_3 at 368 K for 36 hours. Prior to this operation, the base was gradually added to a vigorously stirred $\text{Cr}(\text{NO}_3)_3$ solution at room temperature so that the molar concentration ratio between hydroxide and chromium ions equaled 2.0. The clay suspension described above was added slowly to the vigorously stirred pillaring reagent at 313 K or 343 K and the mixture was stirred for 1.5 or 3.0 hours. Chromia was present in large excess, typically 50-60 mmol Cr/meq clay, to ensure saturation of exchange sites. The products were centrifugated, thoroughly washed with deionized water to remove excess salt, and dried under shallow-bed condition at room temperature. Portions of the materials obtained were heated for 5 h at 673 K under He or H_2 flow.

X-ray powder diffraction patterns were obtained on oriented film specimens prepared in accordance with ref. [8]. Samples were scanned from 2 to 45 2θ on a Philips PW 1120 diffractometer using monochromatized $\text{CuK}\alpha$ radiation and continuous or stepscan methods for peak registration. The IR-spectra were recorded on KBr wafers (10 mg catalyst and 100 mg KBr) with a Specord 80M IR spectrometer. The BET surface area and the pore-size distribution was determined from nitrogen adsorption-desorption isotherms at 77 K (degassing at 393 K, 10^{-4} mbar, 5 h) measured on a conventional volumetric apparatus (Sorpomatic 1900, Carlo Erba Instruments). TGA analysis was carried out with a Setaram TG 85 thermobalance at a heating rate of 6 K min^{-1} in helium flow 30 ml min^{-1} . Chromia content in the samples prepared was determined with electron probe microanalysis (EPM) with a CAM-SCAN analyzer and X-ray fluorescence analysis (XRF).

The 2-propanol and ethanol decomposition was studied in a micro-pulse reactor at 493 K and 623 K, respectively. Prior to the activity test the samples were treated in flowing helium at 673 K for 1.5 h. The reaction products were analyzed with a CVIET-500 M (CIS) gas chromatograph equipped with TCD or FID detector (Porapak Q, 2 m column, heating rate 24 K min^{-1}). First order rate constants for alcohol transformation to hydrocarbons and water were calculated as described elsewhere [9].

The thiophene hydrosulfurization was determined in a microflow reactor with on line GC analysis. Catalyst samples (200 mg) were presulfided in situ in a $\text{H}_2\text{S}/\text{H}_2$ flow (10 mol% H_2S , 60 ml min^{-1}) using the following temperature program: 6 K min^{-1} heating rate from 293 K to 673 K and 2 h at 673 K. Next the reaction mixture consisting of 4.0 mol% thiophene in H_2 was fed through the reactor and was analyzed every 35 min. The reaction conditions were: flow-rate 50 ml min^{-1} , reaction temperature 673K and pressure 1 bar. First order rate constants for thiophene conversion to hydrocarbons (k_{HDS}) and the consecutive hydrogenation of butenes (k_{HYD}) were calculated as described elsewhere [10].

3. RESULTS AND DISCUSSION

3.1. Physical characterization

The X-ray diffraction patterns of air-dried Cr-PILM's prepared from Na- and Ca-montmorillonites pillared at 343 K are shown in Fig. 1a. They are typical for pillared clays [2] and only the first order basal reflections are observed clearly.

Figure 1. X-ray diffraction patterns of Cr-PILM.

A. (1),(3) Cr-(Na)PILM; (2),(4) Cr-(Ca)PILM: (1),(2) pillaring time 1.5 h (3),(4) pillaring time 3.0 h
B. (1),(2) Cr-(Na)PILM pillared at 343K and 373K respectively, (3) Cr-(Na)PILM and (4) Cr-(Ca)PILM preheated at 673K.

The width and intensity of the reflection corresponding to an enlarged basal spacing within the range of 2.3-2.6 nm depends on the parent cationic forms used. The XRD patterns of the samples prepared from Ca-montmorillonite [Cr-(Ca)PILM] exhibit a more intense and narrow peak near 2.4 nm than the samples derived from Na-form [Cr-(Na)PILM] which, in addition usually show a somewhat larger basal spacing (e.g. 2.5-2.6 nm), (see Fig. 1 a, patterns 1 and 2). With respect to the pillaring reaction time, it can be stated that this parameter is more important for Ca-montmorillonite than for its sodium form. For instance, in the case of Ca-montmorillonite increase of the reaction time from 1.5 to 3.0 h results in a basal spacing increasing from 2.4 to 2.6 nm and in reflections of greater intensity in the XRD pattern (Fig. 1a, spectra 2 and 4). Probably this is due to a different rate of ion-exchange reaction between parent cations and chromium oligomers, as well as to the different swelling behaviour of these cationic forms in water medium [11]. As can be seen in Figure 1b (patterns 1 and 2), the increase in pillaring reaction temperature from 313 K to 343 K does not significantly change the basal spacing and the shape of the XRD pattern of samples derived from Na-montmorillonite. The same applies to Cr-(Ca)PILM.

The rate at which the air-dried Cr-PILM samples are heated in He or H₂ strongly influences the structure of the resulting material. When the rate was above 1K min⁻¹, strong amorphization of the structure took place, and only very broad XRD peaks were observed.

This observation is in good agreement with data published by Figueras et al. for Zr-PILC [12]. Heat-treatment at 573-673 K for 5 h in He or H_2 (heating rate: 1 K min^{-1}) results in partial broadening and intensity decrease of the XRD peaks as well as decrease of the basal spacing (see Fig. 1b, spectra 3 and 4). The pillar height as large as 1.11-1.14 nm (estimated by subtracting from basal spacing the thickness of the silicate layer 0.96 nm) was maintained up to 673 K irrespectively of parent cationic form used for Cr-PILM synthesis.

Figure 2 shows the infrared spectra in the region of the lattice vibrations of the parent cationic forms of the montmorillonite, air-dried Cr-(Na)PILM as well as heat-treated (He, 673 K, heating rate 1 K min^{-1}) Cr-(Na)PILM and Cr-(Ca)PILM. Pillaring of the clay leads to a shift toward lower wavenumbers of the bands at $480\text{-}490\text{ cm}^{-1}$ and at $525\text{-}540\text{ cm}^{-1}$ which are assigned to Si-O-Si and Si-O-Al bending vibrations respectively [13,14]. In addition, the relative intensities of these bands are changed upon pillaring (Fig. 2, spectra 1,2 and 4,5).

Figure 2. IR spectra of:
 (1) Na- and (4) Ca-forms of the montmorillonite,
 (2) air-dried Cr-(Na)PILM and
 (5) air-dried Cr-(Ca)PILM,
 (3) Cr-(Na)PILM pretreated at 673 K
 (6) Cr-(Ca)PILM pretreated at 673 K.

Also, the shifts are observed toward higher wavenumbers of the 1110- and 1052- cm^{-1} bands which correspond to Si-O-Si asymmetrical stretching vibrations [14]. Heat-treatment causes the most significant changes in the IR-spectra of Cr-PILM's (see Fig.2, spectra 3 and 6), e.g. the intensity of the Al-OH bending at 630 cm^{-1} decreases and overlapping of the bands at $1110\text{-}1052\text{ cm}^{-1}$ takes place. Also the vibrations characteristic of Al_2OH and $AlMgOH$ modes at 860 and 930 cm^{-1} are affected by heating, as can be seen in Fig. 2. It is believed that protons released during the transformation of pillars from hydroxymetal form to oxidic state can migrate into the octahedral layer of the montmorillonite, and further, hydrolyse the octahedral cations (Al, Mg, Fe) [15]. As a result, the ability of these protons to perturb the librational lattice modes leads to the shift and disappearance of the respective vibrations in the IR spectra. These results reveal some features which reflect interactions of the pillaring reagent and the pillars themselves with tetrahedral layers and protonic attack on the octahedral cations of the montmorillonite upon intercalation and heat-treatment.

The TGA shows that up to 25 wt% of the Cr-PILM's total weight is lost monotonously at temperatures between 363-873 K. This can be ascribed to the loss of water adsorbed on the external surface and in the microspace generated by pillaring. From the data obtained it can be concluded that dehydration behaviour of the samples studied is similar to other PILC's e.g. AL-PILC [15]. Nitrogen adsorption-desorption isotherms determined at liquid nitrogen temperatures are shown in Figure 3a.

Figure 3. (A) Adsorption-desorption isotherms of N₂ on: (1) air-dried Cr-PILM, (2) Cr-PILM pretreated at 673 K and (B) pore size distribution of these catalysts.

The hysteresis loop observed in the desorption isotherm is attributed to materials with slit-shaped [16] mesopores which is to be expected when a layer structure is expanded by means of pillaring [17]. The materials exhibit a narrow mesopore size distribution with maximum at 2.0-2.1 nm (Fig. 3b). The adsorption isotherms of the products prepared from both cationic forms of montmorillonite fit the BET equation in the relative pressure range 0.05-0.30 which was used for calculation of the surface areas. Heat-treatment in helium flow at 673K leads to a decrease in the BET surface area by 46-49 m²g⁻¹ irrespective of the parent form used for Cr-PILM synthesis but has no significant influence on the mesopore size distribution (see Fig. 3b).

The representative samples with properties listed in the Table 1 were chosen for the catalytic tests.

Table 1

Basal spacing (nm), textural properties and chromia content for Cr-PILM's studied

Sample	Treatment temperature K	d ₀₀₁ nm	S.A. BET m ² g ⁻¹	V microp. cm ³ g ⁻¹	Cr ₂ O ₃ wt %
Cr-(Na)PILM	298	2.63	286	0.124	39.4
Cr-(Na)PILM	673	2.07	241	0.102	
Cr-(Ca)PILM	298	2.54	357	0.126	36.6
Cr-(Ca)PILM	673	2.10	308	0.11	

3.2. Catalysis

The decomposition of 2-propanol and ethanol is the typical reaction for investigating the acid-base properties of heterogeneous catalysts [18]. In the case of these alcohols, catalysts can be classified with regard to their propensity for dehydration or the dehydrogenation reactions resulting in propene or acetone (2-propanol) and ethene or acetaldehyde (ethanol). The results which are shown in Figure 4 indicate that in the presence of Cr-PILM's dehydration is the main reaction pathway in the case of 2-propanol.

Figure 4. Decomposition of the 2-propanol as a function of time for Cr-PILM
 Δ = 2-propanol conversion,
 $\blacksquare$ = acetone, $\bullet$ = propene.

Figure 5. Ratio of the rate constants for dehydrogenation (k_d) and dehydration (k_p) of the ethanol over (1), (2) Cr-PILM, (3) Cr-PILM with 5 wt % of free Cr_2O_3 .

Initially, all samples exhibit acetone formation in trace amounts. However, the dehydrogenation activity decreases rapidly to a level much lower than that of dehydration. Although ethanol showed the same overall picture, the dehydrogenation activity was found to be higher and more stable in this case. This difference might be due to the difference in reaction temperature (2-propanol: 493 K; ethanol: 623 K). Based on these findings the following assumptions can be made:

- (i) the number of basic sites of Cr-PILM is small or their strength is weak;
- (ii) the basic sites were self-poisoned by water formed from alcohol molecules;
- (iii) the dehydrogenation activity of the Cr-PILM samples is low in comparison with bulk Cr_2O_3 due to grafting of the chromia pillars to the silicate layers.

The first assumption is being studied now and results will be presented later. The poisoning of the basic sites by water formed from alcohols was shown for highly dehydrated silica by Matsumura in ref.[19]. It is possible that the same phenomenon takes place in the case of chromia pillared montmorillonite.

The third assumption was verified by catalytic testing of a specially prepared Cr-PILM containing 5 wt. % free and unhomogeneously distributed chromia (EPM results, peak at $36\ 2\theta$ in XRD pattern). For this sample the ratio of the dehydrogenation and dehydration rate constants ($r = k_d/k_p$) is higher than that observed for Cr-PILM with homogeneous distribution of chromia (see Fig. 5). This means that the presence of chromia on the external surface of the clay particles leads to an increase in dehydrogenation activity, which, in turn, is indicative for the non-uniform distribution of the active phase throughout the pillared material.

As mentioned in the experimental section the Cr-PILM samples were also subjected to a thiophene HDS activity test. In this respect, it is important to note that heat treatment of air-dried Cr-PILM results in the conversion of chromia oligocations to chromia pillars and that this process should be accomplished in the absence of air [2]. At present, it is not clear which gaseous medium is the most appropriate from the HDS catalysis point of view. Therefore, H_2 which is possibly capable of (partial) reduction of chromia or an inert gas (He) were used here. Figure 6 shows the thiophene HDS and butene hydrogenation (HYD) activity of the samples preheated in H_2 or He at 623 K for 5 h prior to sulfiding in H_2S/S .

Figure 6. Reaction rate constant for thiophene HDS (●) and butene HYD (○) as a function of time-on-stream : (1) Cr-PILM pretreated in He, (2) Cr-PILM pretreated in H_2 .

Figure 7. Reaction rate constant for thiophene HDS as a function of time-on-stream : (●), (+) presulfided Cr-(Ca)PILM (1) and Cr-(Na)PILM (2), (▲), (◆) oxidic forms of these catalysts.

All H_2 pretreated samples exhibit a lower initial and steady state activity for both reactions. At present we do not have enough information about the chromia containing phase generated during the H_2 pretreatment to explain this phenomenon.

Figure 7 shows the thiophene HDS as a function of run time for the oxidic and presulfided Cr-PILM's. The activity of the presulfided samples is very high and decreases slowly with increasing run time. Interestingly, the activity of the oxidic samples goes through a maximum at about 30 minutes run time but remains considerably lower during the entire test run. A similar behaviour was observed for samples prepared from different parent cationic forms of the montmorillonite. The same phenomenon was reported by de Beer et al. [20] for alumina supported $CoO-MoO_3$ and MoO_3 catalysts. These results clearly show that reaction with H_2S activates the Cr-PILM catalysts most likely by formation of chromium (oxy) sulfides. This is in line with the color change of samples from grayish-green to black as a result of presulfidation. The butene HYD changed more or less parallel the HDS activity (see Fig.6). The high butene HYD activity observed for Cr-PILM is in good agreement with results obtained previously by Vissers et al.[21]. The presulfided Cr-PILM's show a remarkable activity for thiophene HDS and the consecutive reaction of butene hydrogenation during prolonged (up to 24 hours) catalyst testing.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to E.M. van Oers for adsorption measurements and to Dr. W.R.A.M. Robinson for his advice and help. Thanks are also due to V. Dzygun and N. Kostoglod for their help.

These investigations are supported in part by the Netherlands' Foundation for Chemical Research (SON) with financial aid from the Netherlands' Technology Foundation (STW).

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