Synthesis of Al-pillared beidellite and its catalytic activity in the hydroconversion of *n*-heptane

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Received 15 March 1994; accepted 13 September 1994

Aluminum-pillared clays based on synthetic beidellite have been prepared by exchanging hydrothermally synthesized beidellite with partly hydrolyzed aluminum nitrate solution followed by calcination. It is shown that a catalyst containing 50 wt% amorphous silica and 50 wt% pillared beidellite loaded with 0.8 wt% Pt has an *n*-heptane hydroconversion comparable to a commercially available silica–alumina and does not significantly deactivate with increasing time on stream (within 14 h).

Keywords: beidellite; Al-pillared clays; *n*-heptane hydroconversion

1. Introduction

High surface area two-dimensional zeolitic molecular sieve catalysts can be prepared by interlayering (or pillaring) smectites with inorganic polyoxohydroxy cations especially from Al [1–4] and Zr [5–7]. Recent studies have provided details on the synthesis and characterization of Na-beidellite, a dioctahedral 2 : 1 smectite clay [8,9], and its aluminum-pillared analogue [3,4,10,11]. Compared to nat-

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ural clays, synthetic clays have the advantage of high purity and controllable composition, e.g. varying the substitution of Si by Al in the tetrahedral sheet influences the acidity. Because of the acidity of pillared beidellite, it is interesting to study the catalytic activity and selectivity for *n*-heptane hydroconversion. This reaction is thoroughly studied on Pt-loaded zeolites and other commercial catalysts. Therefore, it is interesting to compare the results of the pillared beidellite with those of one of the commercially available catalysts, amorphous silica–alumina ASA (American Cyanamid), which is used as a type of standard in the KSLA laboratory.

2. Experimental

2.1. MATERIALS

The starting clay was a Na-beidellite hydrothermally synthesized according to the method described by Kloprogge et al. [8,9]. A gel with composition $Na_{0.7}Al_{4.7}Si_{7.3}O_{22}$ was hydrothermally treated for fourteen days at 350°C and 1 kbar in a Tuttle-type externally heated, cold-seal pressure vessel. The Na-beidellite has a cation exchange capacity (CEC) of approximately 70 meq/100 g [8]. The Al polyoxocation was prepared by forced hydrolysis of 0.5 M $Al(NO_3)_3$ solution (Merck no. 1063) with 0.2 M NaOH solution (Merck no. 6498) at 23°C, until a molar ratio OH/Al of 2.4 was reached [12]. An amount of hydrolyzed Al solution, equivalent to 30 meq Al/g clay, was added to the 2 wt% beidellite slurry and allowed to react for 16 h, followed by repeated washing and calcination at 500°C. The beidellite and its pillared analogue were characterized by means of X-ray powder diffraction (XRD) using a Philips PW 1050/25 diffractometer (Cu Kα) and chemical analyses were obtained by dissolution of the clay using lithium-borate fusion and subsequent analysis of the solution with inductively coupled plasma–atomic emission spectroscopy (ICP-AES). BET surface areas have been determined by N_2 adsorption using a Carlo Erba Sorptomatic 1800.

2.2. CATALYST PREPARATION

The pillared beidellite was impregnated with a mixture of H_2PtCl_6 equivalent to 0.8 wt% Pt on the clay and HNO_3 solution for 1 h. The platinum was reduced by heating in air for 1 h at 500°C. An amount of 150 mg of a homogeneous mixture containing 50 wt% amorphous silica and 50 wt% pillared beidellite loaded with Pt, grain size 40–100 mesh sieve fraction, was used in a standard type hydroconversion experiment using H_2 as carrier gas (flow rate 2.24 Nml min^{-1}), *n*-heptane flow rate 0.15 g h^{-1} and a WHSV of 1020 Nml g^{-1} h^{-1}. Before starting the reaction the catalyst was reduced in the reactor by heating to 400°C at 1.5°C min^{-1} and kept at that temperature and a pressure of 30 bar for 2 h. The reaction was carried out for 14 h at 350°C and 30 bar. The reaction products were identified with a gas chromatograph. A comparison is made with similarly Pt-loaded commercially available silica–alumina (ASA) containing 50 mol% SiO_2 and 50 mol% Al_2O_3 (American Cyanamid).

3. Results and discussion

X-ray diffraction patterns of beidellite and its Al-pillared analogue show an increase of the basal spacing from 12.4 to 18.4 Å after intercalation at 25°C, which decreases to 16.4 Å after calcination at 500°C (fig. 1). Table 1 shows the clay composition before and after pillaring indicating the presence of approximately 1 pillar per 7 unit cells. The BET surface area increases from 65 to 345 m^2/g upon pillaring. This increase is totally due to the enlargement of the internal (microporous) surface area caused by the expansion of the interlayer space between the clay sheets. The amount of interlayer water based on weight loss after heating to 150°C is rather variable for various beidellite samples. The chemical analysis indicates some aluminum on the interlayer position together with a slightly increased Al–Si substitution. This is in contrast with the findings of Kloprogge et al. [8] and Kloprogge [11], who found compositions consistent with the gel composition. A possible explanation is the presence of some amorphous silica accompanying the beidellite.

Fig. 2 displays the hydroconversion activity and selectivity for iso-C_7 for 50 wt% Pt-loaded Al-pillared beidellite and ASA as calculated from the amounts

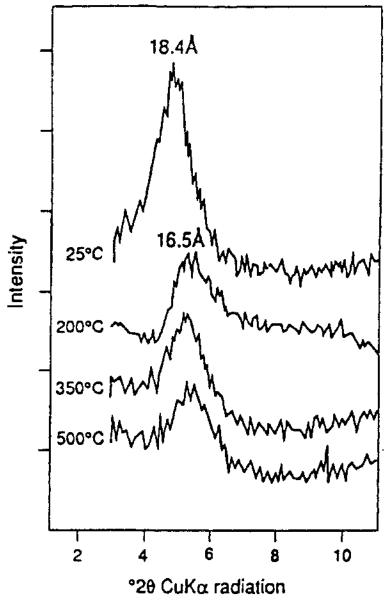

Fig. 1. XRD powder pattern of pillared beidellite after calcination at various temperatures.

Table 1
Chemical analyses (wt%) of the synthetic beidellite and its pillared analogue

	Beidellite	Pillared beidellite
SiO_2	50.59	36.49
Al_2O_3	30.51	43.66
Na_2O	2.63	–
H_2O[a]	8–14	15.29
total[b]	91.94–99.18	95.44

	Structural formula
beidellite	$(Na_{0.71}Al_{0.08})Al_{4.00}(Si_{7.05}Al_{0.95})O_{20}(OH)_4$
pillared	$[Al_{13}]_{0.14}Al_{4.00}(Si_{7.05}Al_{0.95})O_{20}(OH)_4$

[a] Based on weight loss during heating at 150°C of various beidellite samples.
[b] Depending on the amount of water.

of the reaction products. The Al-pillared beidellite catalyst was diluted with 50 wt% amorphous silica because a 100 wt% sample gave complete conversion and nothing could be concluded about its behaviour, deactivation and coke formation, with increasing runtime. The conversion of the 50 wt% Al-pillared beidellite is initially slightly higher than that of pure ASA and becomes almost constant at 35%, while the selectivity for iso-C_7 is slightly lower. Poncelet and Schutz [13] have shown that Al-pillared beidellite loaded with Pt is more active than Al-pillared montmorillonite loaded with Pt due to the stronger Brønsted acidity of the former. These authors observed the catalytic activity to be comparable for pillared beidellite and zeolite, but the selectivity of the pillared beidellite to be higher. The high catalytic activity of the catalyst containing only 50 wt% Al-pillared beidellite cat-

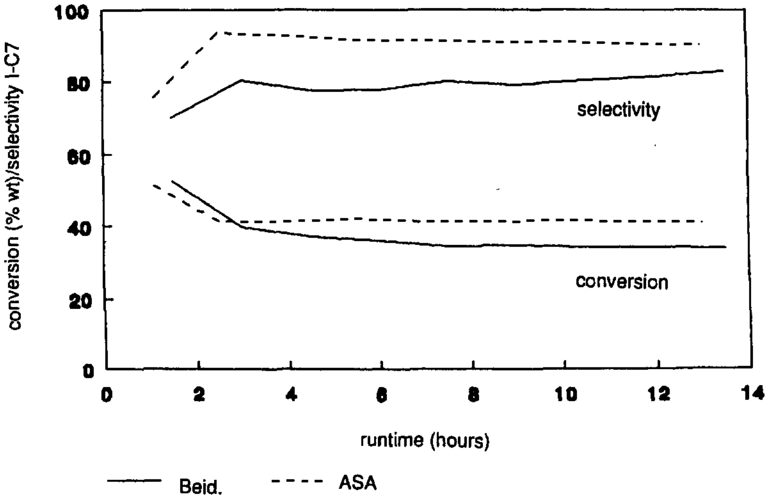

Fig. 2. Hydroconversion activity and selectivity for iso-C_7 for amorphous silica/Pt-loaded pillared beidellite and pure silica–alumina ASA.

alyst is attributed to the moderate acidity, mainly being of the Brønsted type, which was confirmed by our pyridine adsorption measurements. Our results prove that Pt-loaded Al-pillared beidellite is an interesting hydroconversion catalyst at intermediate temperatures with activity and selectivity comparable to commercial catalysts like silica/alumina.

Acknowledgement

The authors are grateful to A.M.J. van der Eerden for his help in the HPT Laboratorium and H. de Jonge, Koninklijke/Shell Laboratorium Amsterdam, for performing the hydroconversion experiments. E. Booy especially thanks Professor R. van Veen, who gave the opportunity to perform a part of his research at Koninklijke/Shell Laboratorium Amsterdam.

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