A Convenient Procedure for the Acidic Activation of Mineral Bentonite: An Environmentally Friendly Method for the Preparation of Bleaching Earths

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Refluxing montmorillonite-containing raw bentonite ($(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2$) in aq HNO_3, then neutralizing it with NH_3 produces NH_4NO_3-containing NH_4–bentonite. The NH_4NO_3 intercalated can be eliminated as a gaseous product (N_2O and H_2O) by heating at 400 °C, and the deammoniation and dehydroxylation process of the preactivated bentonite leads to formation of bleaching earth ($H_x(Al,Mg)_{2-y}Si_4O_{10}(OH)_2$).

Acid-activated bentonites (bleaching earths) are widely used absorbents in the food industry.[1] Various methods have been developed for their preparation, mainly by using HCl or H_2SO_4 as activation agent.[2] These technologies produce large amounts of acidic wastewater which require alkaline neutralization and may be the cause of environmental salt-burdening.[3]

Based on our previous work,[4] a new process involving nitric acid preactivation, ammoniacal neutralization and a heat treatment has been developed. Aqueous washing, consequently the acidic wastewater formation, has been eliminated. Mineral bentonite was preactivated in a 20% aq HNO_3 by refluxing for 3 h. The preactivated bentonite formed in this process has no excellent bleaching property,[5] although the layered structure has already been destroyed during this treatment (Figure 1). The intense XRD reflection corresponding to the basal spacing laminar clay structure ($d_{001} = 1.520$ nm, scan 1) disappeared (scan 2), and only minor changes could be detected after the heat treatment (scan 3). The preactivated sample contains a small amount of residual HNO_3 ($\nu_{NO} = 1380\,cm^{-1}$) which, however, is eliminated by the heat-treatment of the activated bentonite to remove the NH_4NO_3 formed during the ammoniacal treatment. The decomposition temperature of the NH_4NO_3 intercalated in the preactivated sample is 260 °C, which shows the absence of any catalytic effects of the aluminosilicate cage of the preactivated bentonite.

$$NH_4NO_3 = N_2O + 2H_2O \qquad (1)$$

Only gaseous N_2O ($m/z = 44$) and H_2O ($m/z = 18$) are formed; NO_x gases and NH_3 do not evolve (Figure 2).[6] The small peak at 100 °C refers to the elimination of the physically adsorbed water.

As the sign of the dehydroxylation/deammoniation processes an extended water/NH_3 elimination step ($m/z = 18$ (H_2O) and $m/z = 17$ (NH_3)) has occurred between 300 and 400 °C. A well-defined peak of N_2 ($m/z = 28$) could be observed at 310 °C (without any NO ($m/z = 30$) or N_2O ($m/z = 44$) formation) as a consequence of the decomposition of the adsorbed ammonia. According to these processes, heating at 400 °C improves the bleaching activity. The comparison of the IR spectra of the raw, the preactivated and the heat-treated bentonites shows that the intensity and the position of the bands assigned to M–OH (M = Al, Mg, and Fe) bonds ($\approx$1100, $\approx$900, and $\approx$840 cm^{-1}) of octahedral sites are shifted and decreased. This confirms the role of the dehydroxylation in the final activation step. After the heat treatment of the bentonite no coordinated ammonia peaks could be detected in the IR spectrum. The deammoniation and the dehydroxylation processes liberate the active sites, via partial dealumination as it was observed in the case of zeolites.[7] Surface area and pore distribution studies confirm the appearance of new active sites. The specific surface areas of the

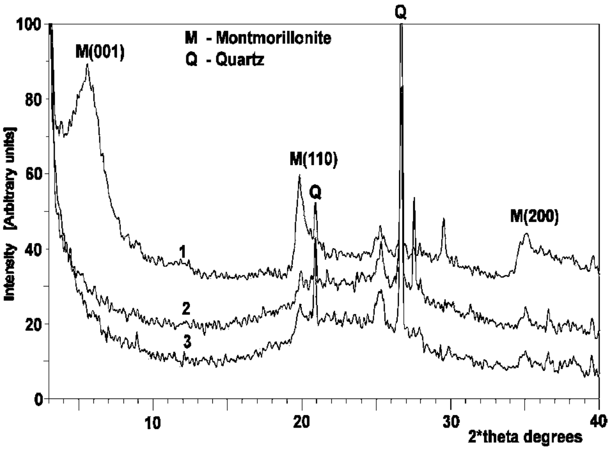

Figure 1. XRD (Cu Kα) of raw (1), HNO_3 preactivated (2) (acidic) and post heat-treated (3) bentonites.

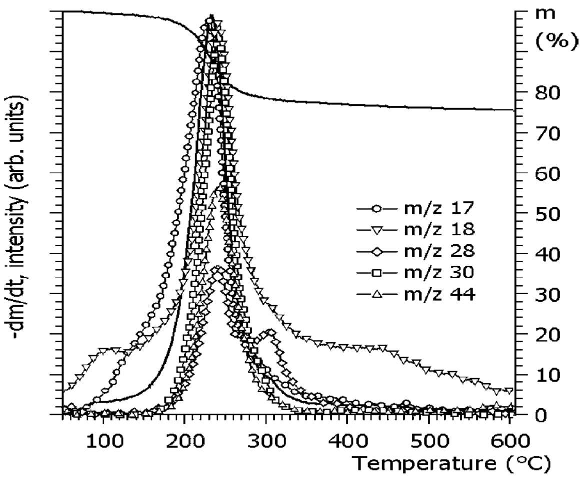

Figure 2. TG-MS of HNO_3-activated and NH_3-treated bentonite sample.

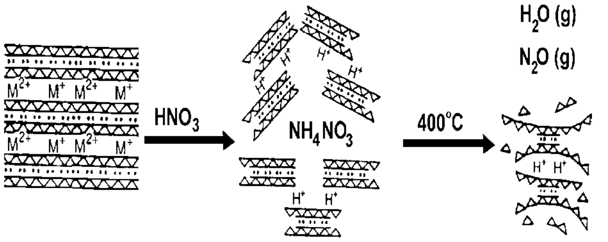

Figure 3. Schematic representation of the bentonite activation procedure.

raw, preactivated and heat-treated samples were 130, 332, and 361 m^2/g, respectively.[8,9]

Activation at higher temperatures or longer heating time led to complete dehydroxylation and loss of the bleaching capacity. The two-step activation process including nitric acid activation and subsequent thermal treatment (Figure 3) is a new kind of bentonite activation methods. The structural changes, however, are almost the same as in the case of traditional hydrochloric and sulfuric acid treatments. Similarly to the HCl treatments[10] N_2 adsorption isotherms show the change from H3 to H2 type of hysteresis induced by transformation of the slit-shaped pores into ink-bottle pores. It is the consequence of the destruction not only of the octahedral but the tetrahedral sheet as well, when silica (800 and 470 cm^{-1}) is formed (which deposited at the mouth of pores producing ink-bottle pore type). Pore distribution measurements show the presence of mesopores between 1.6 and 3.3 nm depending on the type of the starting raw bentonite. The presence of the pores $<$15 Å could be excluded. Our process using nitric acid activation which is then followed by ammoniacal treatment and heating at 400 °C has proved to be a convenient method to produce highly active bleaching earths. Wastewater formation is eliminated, and the N_2O in the flue gas can be decomposed in a catalytic converter.[11] The method is environmentally friendly and produces bleaching earth comparable in quality with the common hydrochloric-acid-activated bleaching earths and superior to the sulfuric acid activated ones.

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