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Preparation of TiO_2-pillared montmorillonite as photocatalyst Part I. Microwave calcination, characterisation, and adsorption of a textile azo dye

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ABSTRACT

Two photocatalysts based on TiO_2-pillared intercalated montmorillonite have been prepared by microwave for 10 min at 700 W or by furnace heating at 673 K. Montmorillonite pillaring with TiO_2 increased the basal spacing to 14.7 Å (conventional heating) and 17.6 Å (microwave heating). XRD patterns of both materials showed the presence of 100% anatase with a slightly higher rate of crystallinity obtained through microwave calcination than by conventional heating at 673 K. The BET specific surface area of the microwave prepared photocatalyst (151 $m^2\ g^{-1}$) was 3 fold higher than those of the Degussa TiO_2 P25. At pH = 5.8, the maximum adsorption capacity of Solophenyl red 3BL (a textile azo dye) on the TiO_2-pillared montmorillonite calcined by microwave was 185 mg g^{-1}, whereas it was 1.4 and 3 fold lower on the TiO_2-pillared montmorillonite calcined at 673 K, and on the Degussa TiO_2 P25 respectively. The influence of pH on the adsorption of the dye depended on the pH_{ZPC} of the pillared montmorillonites.

1. Introduction

Many toxic and hazardous compounds are efficiently degraded by heterogeneous photocatalysis. The use of titanium dioxide as photocatalyst for air and water treatment is well documented as well as the fundamental mechanisms of the process (Bahnemann et al., 1994; Hermann, 1995, 1999; Konstantinou and Albanis, 2004). The main primary step is the adsorption of the substrate on the support. Thus, efforts have been carried out on the synthesis of new materials having high specific surface area, low particles size with the highest expected photoreactivity (Cappelletti et al., 2008). Nevertheless, the practical recovery of the powder when used in aqueous suspension, still remains difficult. Supported TiO_2 on different minerals or TiO_2 thin films appeared as a way to overcome the recovery problem and also to enlarge the application fields (Ho et al., 2007). Mesoporous materials which can be easily separated from the treated effluent, have been synthesized, and demonstrated their feasibility for photocatalytic treatment of wastewaters especially toward azo dyes (Xu and Langford, 1997; Yang et al., 1998; Zhu et al., 2005; Li et al., 2007). They are mainly based on clay minerals, zeolites, silica or activated carbons. Among them, pillared clays (PILCs), constitute a group of mesoporous materials (Yoneyama et al., 1989; Vicente et al., 2001; Valverde et al., 2002). The intercalated polycations obtained by hydrolysis of Ti^{4+} cations, closely depend on the nature of the acidic medium (Del Castillo et al., 1997). One of the main stable species is expected to be $[(TiO)_8(OH)_{12}]^{4+}$ (Vicente et al., 2001). This polycation forms titanium oxide through calcinations, leading to a two-dimensional porous network with interesting textural and chemical properties for catalytic and adsorption applications (Ohtsuka, 1997; Tomlinson, 1998). Experiments carried out with titanium alkoxide $Ti(OC_3H_7)_4$, hydrolysed in HCl lead to a material with 280 $m^2\ g^{-1}$ specific surface area and a 23.1 Å basal spacing (Yamanaka et al., 1987). Specific surface areas and basal spacing of TiO_2-pillared montmorillonite are in the range 128–350 $m^2\ g^{-1}$ and 18–24 Å (Yamanaka et al., 1987; Bernier et al., 1991; Khalfallah Boudali et al., 1994; Del Castillo et al., 1997). Compared to very toxic $TiCl_4$, the use of titanium alkoxide is attractive to synthesize TiO_2-pillared montmorillonites. In addition, the properties are expected to be different according to the nature of the Ti precursor used. The best precursor was $Ti(OC_2H_5)_4$ leading to a polymeric structure after hydrolysis and condensation of the previous titanium alkoxide according to an optimum molar ratio $HCl/Ti(OC_2H_5)_4 = 2$ (Del Castillo et al., 1997). A final specific surface area of 334 $m^2\ g^{-1}$ and a 25.5 Å basal spacing were found after calcination at 373 K. As the calcination temperature increased from 373 to 773 K, the specific surface area and the basal spacing decreased to 311 $m^2\ g^{-1}$ and 18 Å respectively.

Many papers and reviews were published on the fundamental mechanisms of the photocatalytical degradation process and mentioned that the primary step is the adsorption of the substrate on the support (Zhang et al., 1998; Bahnemann et al., 1994; Houas et al., 2001; Konstantinou and Albanis, 2004). The second step concerns the

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