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Control of micropore size in supermicroporous titania–chromia system TiO_2–Cr_2O_3

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Abstract

Sol–gel hydrolysis reactions of titanium(IV) isopropoxide and chromium (III) acetate hydroxide in the presence or absence of propanol, using the following amines as structure directing agents; *N*-hexylamine, *N*-methylhexylamine, and *N*-propylbutylamine, yielded microporous mixed metal oxides with the presence of pores largely in the 10–20 Å region, and surface areas that vary from 564 m^2/g when *N*-hexylamine is employed as pore directing template to 494 m^2/g when *N*-propylbutyl amine is employed as template. The maxima in pore size distribution increases with increase in steric crowding around the nitrogen in the alkyl amine. In addition, the nitrogen adsorption–desorption isotherm shifted from Type 1 isotherm when *N*-hexylamine is used as templating agent to Type 4 isotherm in *N*-propylbutylamine.

Keywords: Hexylamine; Pore; Titania; Chromia; Sol–gel hydrolysis

The well known zeolites, microporous crystalline aluminosilicates exhibit uniform pore size distribution, high thermal and hydrothermal stability, and a wide spectrum of acidities and shape selectivity [1–3]. These properties permit a broad range of applications for zeolites, that include ion exchangers, sorbent materials and selective catalytic applications. However, the limitation in the pore size and channel dimension (generally less than 9 Å), has restricted their applications in wider areas of catalysis, especially involving bulky organic molecules. In addition, the reactivity of the elements that make up the zeolites, particularly of the Al–O and Si–O bonds, limits their operating pH range between 2 and 12. The use of surfactants with moderately long alkyl chain lengths are known to yield mesoporous materials with pore sizes in the 20–200 Å range [2–13]. There is therefore the need to develop a simple method for the synthesis of porous mixed metal oxides with pore sizes in the 10–20 Å. Such material should bridge the pore size gap between the zeolites (<10 Å) and the mesoporous oxides (>20 Å). Clearfield et al. recently reported a general procedure for making such super-microporous mixed metal oxides starting from metal alkoxides or acetates and *n*-alkylamine as templates using propanol/water mixture as solvent (14). In this report, a direct relationship between the maxima in pore size distribution and the hydrocarbon chain length in the *n*-alkylamine was reported. Using six, seven, eight, nine and ten carbon chain primary alkyl amine, they were able to progressively increase the maxima in pore size distribution in the 10–20 Å [14]. Following a slight modification of the procedure reported by Clearfield et al. [14] for the synthesis of microporous mixed chromia–zirconia system, the current investigation shows that such relationship can also be established by varying the steric crowding around the alkylamine. In the present study, the relationship between the following amines: *N*-hexylamine, *N*-methylhexylamine and *N*-propylbutylamine and the maxima in pore size distribution and surface areas in the titania–chromia system is established. In addition, the role of solvent is also investigated

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in this systems. The syntheses of the Cr_2O_3–TiO_2 system was accomplished by reacting a pre-hydrolyzed chromium acetate hydroxide with titanium (IV) isopropoxide in propanol, followed by addition of respective alkylamine, and sequential addition of water–propanol mixture drop-wise over a period of one hour. The solution was left stirring for 24 h, forming a gel, to which additional water was added and refluxed for 24 h. The solid was separated by centrifuge, and dried in an oven at 65 °C. The products obtained using *N*-hexylamine, *N*-methylhexyl amine and *N*-propylbutylamine are labeled **1**, **2** and **3**, respectively [15]. The dried materials were characterized by TGA, FTIR and elemental analysis using an energy dispersive standardless elemental analyzer [15].

The sorption–desorption isotherms for the mixed chromia–titania oxides were obtained using the nitrogen sorption

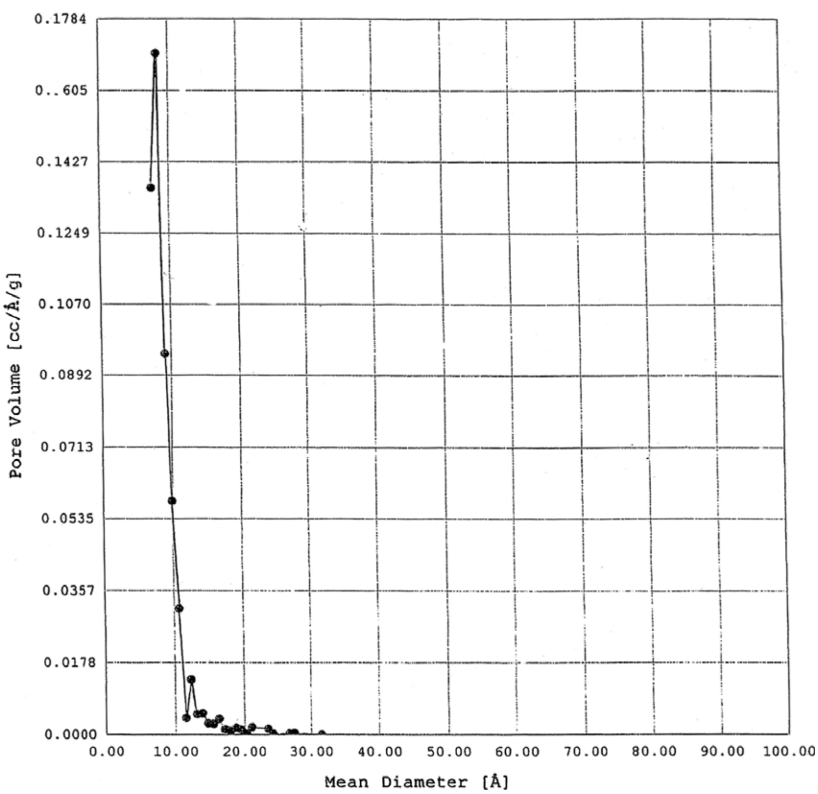

Fig. 1. Pore size distribution curve for isotherm for **1**, as determined by the MP method.

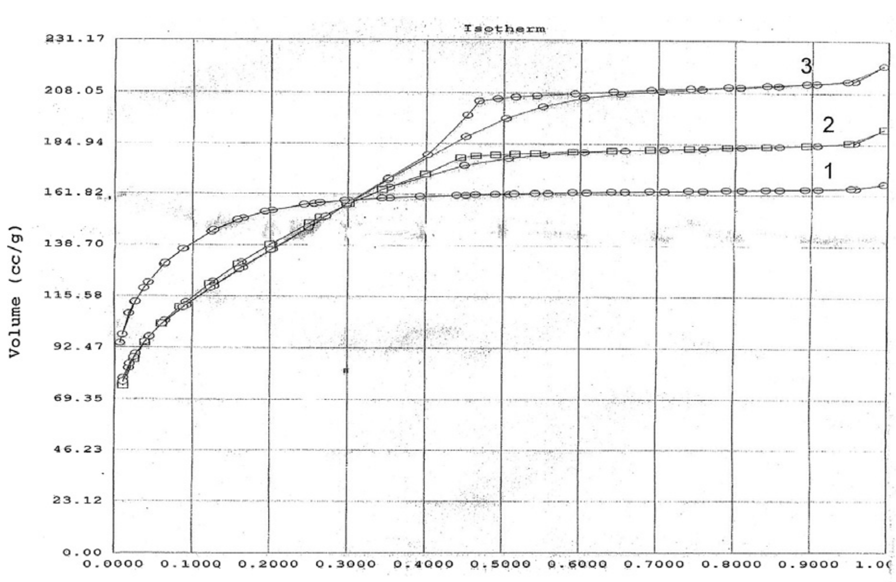

Fig. 2. The N_2 sorption–desorption isotherm for Cr_2O_3–TiO_2 compounds **1**, **2** and **3**.