

BRIEF COMMUNICATION

Synthesis of Porous Chromia-Pillared Tetratitanate

Wenhua Hou, Yashao Chen, Canxiong Guo, and Qijie Yan¹

Department of Chemistry, Nanjing University, Nanjing, 210093, China

Received May 7, 1997; in revised form November 4, 1997; accepted November 10, 1997

The first chromia-pillared tetratitanate is prepared by the reaction of the layered tetramethylammonium-intercalated tetratitanate with an aqueous chromium(III) acetate followed by calcination at 400°C. The new porous material has a specific surface area as high as 94 m² g⁻¹ and an interlayer distance of 1.06 nm along with a moderately strong acidity. The layered nature of the pillared material may be retained above 600°C.

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The formation of porous thermally stable materials by calcination of the intercalated polyhydroxy-cation precursors in layered solids, known as "pillaring," is an important means of obtaining solid acids with catalytic properties (1). Work in this field has mainly been concerned with smectite clays and layered four-valent metal phosphates (2, 3). Recently, it was reported that layered metal oxides based on octahedral framework structures may also be pillared by inorganics such as alumina and silica oxide (4, 5).

TiO₂ has attracted scientific interest for a long time since it has significant and distinctive properties as a catalyst or catalyst support (6). Unfortunately, TiO₂ itself is a weakly acidic oxide and loses most of its acidity upon heating at 500°C. On the other hand, it is well established that layered titanates can be preswollen by organic amines and then pillared by inorganics (4, 7, 8). Chromia is also an interesting inorganic pillar and may contribute new properties to the resultant materials (8–10). However, pillaring of titanate by chromia has never been reported. Here we report the preparation of the first chromia-pillared layered tetratitanate through the intercalation of tetramethylammonium (TMA) and then reaction with chromium(III) acetate [Cr(OAc)₃] followed by calcination. The resulting new pillared product is a porous acidic material with a high thermostability.

K₂Ti₄O₉ and H₂Ti₄O₉ · H₂O (HTi) were prepared according to the literature (7). The (100) reflection at 2θ = 9.8° in the XRD pattern (Fig. 1a) revealed that the obtained HTi

had an interlayer distance of 0.90 nm. Stirring HTi with an aqueous solution of *n*-propylamine at room temperature gave rise to the *n*-propylamine-intercalated HTi (Pr-HTi) with an interlayer distance of ca. 1.73 nm (Fig. 1b). Pr-HTi was further reacted with an aqueous TMA chloride solution at room temperature to obtain TMA-intercalated HTi (TMA-HTi) with an even greater interlayer distance of 1.96 nm (Fig. 1c). An interlayer free gallery of 1.39 nm occupied by intercalated TMA is deduced by subtracting the host layer thickness of 0.57 nm (4). Considering that the TMA ion is spherical with an ionic diameter of 0.53 nm (11), a double layer of TMA ions is thought to be intercalated between the host layers. The interlayer gallery height is a little higher than two times the height of the TMA ion and might be caused by the presence of interlayer water.

Reaction of TMA-HTi with an aqueous Cr(OAc)₃ solution progressively at room temperature, 60°C, and refluxing temperature led to polyhydroxyacetato-Cr³⁺-intercalated HTi (Cr³⁺-HTi) with an interlayer distance of ca. 1.88 nm (Fig. 1d). After calcination at 400°C for 2 h, the organic matter in Cr³⁺-HTi was burned out, leaving chromia-pillared HTi (Cr-HTi). The obtained solid has an interlayer distance of 1.06 nm (Fig. 1e), from which an interlayer free spacing of 0.49 nm was deduced. The layered structure of chromia-pillared tetratitanate is thermally stable above 600°C (see Fig. 1f), whereas HTi is decomposed at 500°C (4). The layered structure of Cr-HTi was collapsed by calcination at 700°C (Fig. 1g). The Cr content in Cr-HTi is ca. 8.7 wt%.

The new pillared product was characterized as a porous material. In comparison, the starting material is nonporous (the specific surface area of K₂Ti₄O₉ is only 5 m² g⁻¹). After calcination at 400°C in air for 2 h, Cr-HTi has a BET surface area as high as 82 m² g⁻¹ along with an average pore diameter of 7.61 nm. It is worth noting that calcination of Cr³⁺-HTi in a N₂ atmosphere may lead to a pillared product with an increased BET surface area of ca. 94 m² g⁻¹ and a somewhat decreased average pore diameter of 4.44 nm. This is similar to the phenomenon

¹To whom correspondence should be addressed.

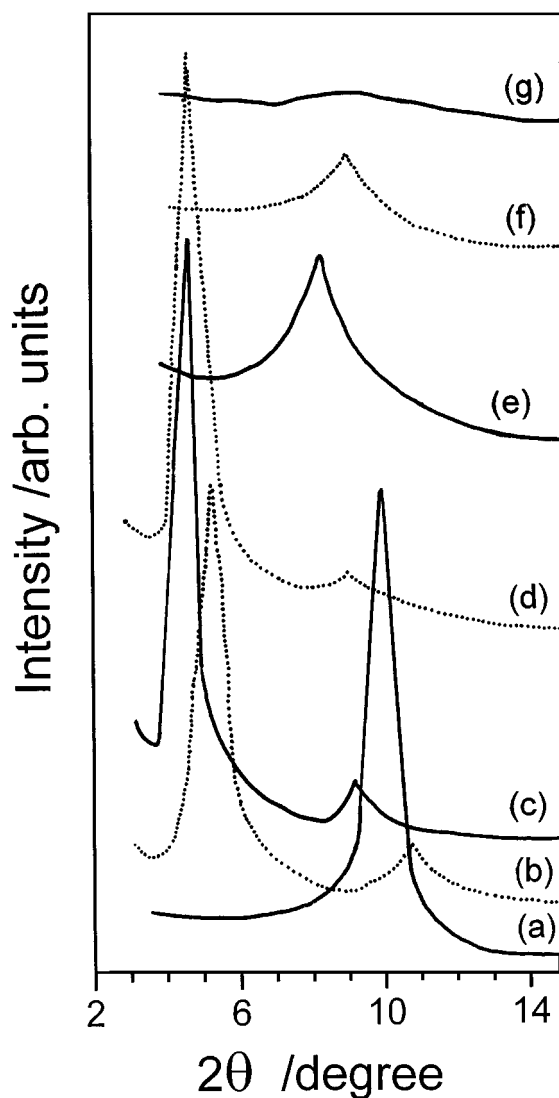


FIG. 1. XRD patterns of (a) as-synthesized $\text{H}_2\text{Ti}_4\text{O}_9 \cdot \text{H}_2\text{O}$, (b) *n*-propylamine-intercalated tetrititanate, (c) tetramethylammonium tetrititanate, and polyhydroxyacetato- Cr^{3+} -intercalated tetrititanate after treatment in air for 2 h at (d) room temperature, (e) 400°C, (f) 600°C, and (g) 700°C.

observed for chromia-pillared α -tin phosphate (10). The appearance of an H3 type hysteresis loop in the N_2 adsorption-desorption isotherm suggests the presence of slit-

shaped pores relates to aggregates of platelike particles of the new material (12). TEM clearly reveals the layered feature of the new material. The adsorption isotherm for the pillared material is classified as type IV in the BDDT classification, which is characteristic of mesopore materials with microporous contributions (13).

Both Brønsted and Lewis acid sites exist in the new material as revealed by the pyridine adsorption in the IR spectrum. Since Cr_2O_3 is known to be a Lewis acid (14), the Brønsted acid sites on Cr-HTi are probably related to the interlayer balance protons. The NH_3 -TPD result indicated that the chromia-pillared tetrititanate (500°C, N_2) is a moderately strong solid acid with a total acid amount of ca. $406 \mu\text{mol g}^{-1}$.

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (NNSFC No. 29573108), the China Postdoctoral Science Foundation, and the Natural Science Foundation of Jiangsu Province is gratefully acknowledged.

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