

Epoxidation with hydrotalcite-intercalated organotungstic complexes

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Abstract

W(VI)-based catalysts for epoxidation were incorporated into hydrotalcite either by anionic exchange or by complexation with phosphonic acids previously incorporated between the sheets. Phenyl- and dodecylphosphonic acids and peroxotungstic salts were intercalated into hydrotalcite as attested by the expansion of the lamellar lattice and the complexation of phosphonic acids with W-peroxo species was made possible when using a lipophilic quaternary ammonium peroxotungstic salt [W(VI)-Aliquat] which maintains the layered structure. These catalysts were checked in the epoxidation of cyclohexene with hydrogen peroxide or *tert*-butylhydroperoxide as external oxidants. The materials prepared by anionic exchange gave only epoxy cyclohexane but with moderate yields, whereas those prepared from previously incorporated phosphonic acids gave rather high selectivity (50–72%) in allylic oxidation products.

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1. Introduction

Tungstates and tungstic acid H_2WO_4 have long been studied in epoxidation reactions with hydrogen peroxide; they behave as oxygen carrier through peroxo species such as $(\text{WO}_5)_n\text{-OH}$ which are formed in the presence of hydrogen peroxide [1]. Heteropoly acids (HPA) with the Keggin structure, $\text{H}_3[\text{PM}_{12}\text{O}_{40}]$ ($\text{M} = \text{Mo}, \text{W}$), were degraded in the presence of excess H_2O_2 to form peroxo species $\{\text{PO}_4[\text{M}(\text{O})(\text{O}_2)_2]_4\}^{3-}$ and $[\text{M}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$. The anionic exchange of W and V onto hydrotalcite has also been known for longtime [2]. The rules of anion exchange of hydrotalcites reported by Miyata [3] made possible to find the conditions for a successful intercalation of anions. For the sake of separation and reuses, tungstate species can be grafted onto several types of carriers such as hydrotalcites by anion-exchange. Tatsumi et al. [4] first reported the preparation of molybdates and tungstates grafted onto MgAl hydrotalcites and tested on epoxidation of olefins. Gardner and Pinnavaia [5] tested a $\text{Zn}_2\text{Al-HT-polyoxometallate}$ solid for the same reactions; $\text{Mg}_2\text{Al-Mo}_7\text{O}_{24}^{6-}$ and $\text{Mg}_2\text{Al-W}_7\text{O}_{24}^{6-}$ were found to be decomposed at 393 K and suggested

that the solids prepared by Tatsumi were salts of general formula $\text{M}_7\text{O}_{24}^{6-}$. Jacobs and co-workers [6,7] introduced tungstates into MgAl [8] and NiAl [9,10] hydrotalcites containing Cl^- anions, prepared under N_2 atmosphere to avoid carbonation and tungsten was introduced as WO_4^{2-} at pH 9, using a competitive anion exchange between tungstates and sulfates or sulphonates in order to obtain a statistical distribution of the anions at the surface [11]. The nature of this competitor anion, added in large excess, determined the interlayer spacing. Hydrophobic samples were obtained by exchanging WO_4^{2-} and *p*-toluenesulfonate; it appeared that oxygen transfer for this solid was carried out easier in a hydrophobic environment and the substrate could easily reach the oxidant. Recently, Mo species have been incorporated into hydrotalcites by different preparation methods and tested in cyclohexene epoxidation [12].

Gardner and Pinnavaia incorporated some polyoxometallates into hydrotalcites through the same anion-exchange process [5]. The exchange of the Keggin type such as $\alpha\text{-}[\text{SiV}_3\text{W}_9\text{O}_{40}]^{7-}$, $\alpha\text{-}[\text{B}^{\text{VI}}\text{VW}_{11}\text{O}_{40}]^{7-}$, $\alpha\text{-}[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ and $[\text{H}_{12}\text{W}_{12}\text{O}_{40}]^{7-}$ onto a zinc hydrotalcite depended on spatial restrictions for replacing NO_3^- anions. These solids lost their lamellar structure between 473 and 523 K, the amorphous state thus reached was stable, and no rehydration was possible.

Organometallic species, such as porphyrins and phthalocyanines, have been also introduced between the sheets of

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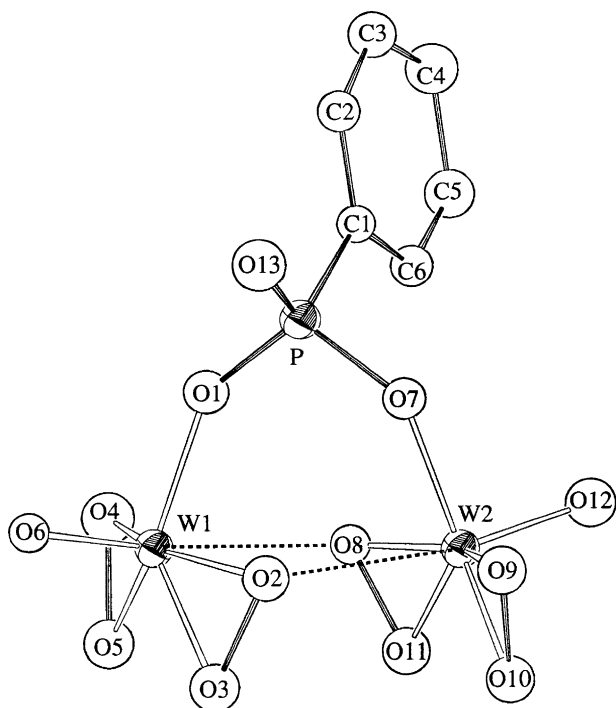


Fig. 1. Phosphotungstate complex.

hydrotalcite and used as oxidation catalysts [8–11]. Phosphonic acids were successfully introduced into the double-layered hydroxide [13].

On the other hand, peroxotungstic acid, a mixture of $\text{H}_2\text{W}_2\text{O}_{11}$ and H_2WO_6 [14], can give complexes with organo-phosphorous ligands such as phosphonic acids $R\text{-PO}_3\text{H}_2$ and phosphoramides $R\text{-P(O)(NRR)}_2$ [15–18]. These complexes are good catalysts in the epoxidation reactions of simple olefins [19] and allylic alcohols [1b] and the structure of the phenylphospho-peroxoditungstic anion, $\text{C}_6\text{H}_5\text{-PO}_3(\text{WO}_5)_2^{2-}$, was shown similar to that of $[\text{PO}_4(\text{WO}_5)_4]^{3-}$ [1b,20] (Fig. 1); the immobilization of these phosphotungstic species was performed by ion-exchange or by covalent bounds to polymeric materials [17–19].

We describe here the insertion into hydrotalcite of the hydrophilic $\text{W}_7\text{O}_{24}^{6-}$ anion and two hydrophobic anionic species, which are derived from the complexation of peroxotungstic acid with phenyl- and dodecylphosphonic acids (Fig. 1).

2. Experimental

2.1. Materials

$\text{Al}(\text{NO}_3)_3$ 98%, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 99%, Na_2WO_4 99%, H_2O_2 30% aq. and TBHP 5–6 M were obtained from Aldrich. NaOH, phenylphosphonic acid ($\geq 97\%$), pentaethylene glycol ($\geq 97\%$), glycerol ($>99\%$) and Aliquat 336 (methyl-trioctyl-ammonium-bromide) were obtained from Fluka. Methanol (98%, Aldrich), 1,2-dichloromethane (99.6%, Aldrich) were used as solvents. Cyclohexene (99%, Aldrich) was used as supplied.

2.2. Preparation of the hydrotalcite and meixnerite

Hydrotalcites were prepared by coprecipitation at 338 K and pH 9 according to procedures described earlier [21]. (a) 0.67 mol/L of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.33 mol/L of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (for a ratio Mg/Al = 2) and (b) 2 mol/L of NaOH and 0.5 mol/L of Na_2CO_3 were introduced by two electric pumps into a 4-L flask and mixed under vigorous stirring. The mixture was aged at 338 K for 18 h under stirring. The precipitate was washed several times until the solution was free of chloride ions (AgNO_3 test), then dried at 393 K.

Meixnerite was obtained by calcination of hydrotalcite at 723 K in a flow of nitrogen at 1 K/min for 12 h, then cooled and put in deionized and decarbonated water and stirred under nitrogen for 12 h (type-1 suspension).

2.3. Preparation of the tungstate catalysts

The impregnation procedure was used with two kinds of supports: a meixnerite, MX (type-1 suspension) or a carbonated hydrotalcite HT (type-2 suspension). Solutions of different molarities of $\text{Na}_2\text{W}_7\text{O}_{24}$ were obtained from equimolar amounts of WO_3 and Na_2WO_4 , the pH being maintained at 7. A suspension of MX or HT in these solutions was stirred for 16 h, filtered, washed with water and dried at 393 K to give HT-W, MX-Wa and MX-Wb catalysts.

These preparations are illustrated in Fig. 2 and the data reported in Table 1.

2.4. Preparation of the phosphonatotungstate catalysts

Dodecylphosphonic acid was prepared according to procedures described elsewhere [22]. A suspension of carbonated hydrotalcite (1 g) and of phenylphosphonic acid or dodecylphosphonic acid (0.1 mol) was stirred for 36 h and then centrifuged, washed with water and dried at 333 K to give HT-P or HT-D, respectively (Scheme 1). The same procedure was followed with a suspension of meixnerite (1 g) in water (1 L) containing glycerol (100 mL), pentaglyme (100 mL) and phenylphosphonic or dodecylphosphonic acid (0.1 mol); MX-P and MX-D were obtained, respectively. Glycerol and pentaglyme are supposed to favour the expansion of the lattice and facilitate diffusion.

A 0.9 M solution of peroxotungstic acid was prepared by suspending 25 g of WO_3 in 30% hydrogen peroxide (100 mL) and stirring for 5 h at 313 K; the turbid solution was centrifuged. Aliquat (5 mmol) was dissolved in 200 mL water and 5 mL of the peroxotungstic acid solution was added dropwise and the suspension stirred overnight; the mixture was extracted with 50 mL dichloromethane, the extract was washed with water and dried with sodium sulfate, evaporated and the waxy residue was vacuum-dried at room temperature for 4 h to give the peroxotungstate salt $(\text{Oct}_3\text{MeN})_2\text{W}_2\text{O}_{11} \mathbf{6}$ (Scheme 2).

The final catalytic materials were obtained by treating MX-P or MX-D with a solution of the salt **6**: 275 mg of the salt **6** was dissolved in 10 mL dichloromethane and the meixnerite

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