The Reason Why K10 is an Effective Promoter for *meso*-Tetraalkylporphyrin Synthesis

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(Received March 10, 1995)

The reason why K10 is an efficient promoter for porphyrin synthesis is found to be due mainly to the mesoporosity rather than to the acid property of K10, by comparing K10 with progressively acid-treated montmorillonites.

Recently we found that commercially available montmorillonite K10 (sulfuric acid-treated clay) gives *meso*-tetraalkylporphyrins in high yields from aliphatic aldehydes and pyrrole.[1] For example, a yield of *meso*-tetrapentylporphyrin was increased to 46% by using K10, whereas the use of conventional acids, CF_3CO_2H and $BF_3{\cdot}OEt_2$[2] gave the porphyrin in 15-20% yield. This communication will unveil the reason why K10 is so effective for porphyrin synthesis.

Brown et al. reported that sulfuric acid treatment on montmorillonite changes the structure of the clay in laminated to mesoporous forms.[3] Therefore, we prepared sulfuric acid-treated montmorillonites (SA-Mont) in a similar way to the preparation of K10, and applied the SA-Mont to porphyrin synthesis in order to investigate how the acidity and porosity of the clays are responsible for the porphyrin yields.

Highly purified Na-montmorillonite, Kunipia F (purchased from Kunimine Co.) was used as a parent clay. Ten grams of Na-montmorillonite (Na-Mont) was added to 800 ml of a 30% H_2SO_4 aqueous solution. The resulting clay suspension was vigorously stirred under reflux for the given time. Then the SA-Mont was washed thoroughly with deionated water until pH of the filtrate became higher than 6.5, and dried at 60°C in air.

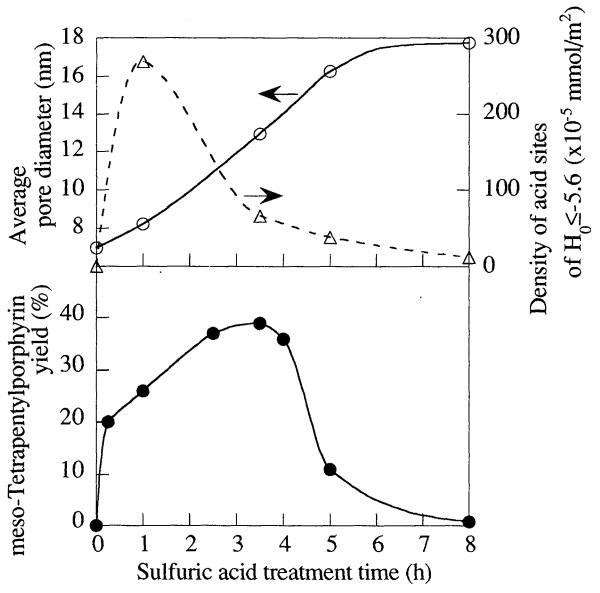


Figure 1. The dependence of *meso*-tertrapentylporphyrin yield (●), the average pore diameter of the SA-Mont (○) and the density of acid sites of $H_0 \leq -5.6$ on the clay surface (△) on sulfuric acid treatment time.

The surface acidity of the SA-Mont was measured in CH_2Cl_2 by using Hammett indicators,[4] anthraquinone (pKa=-8.2), bezalacetophenone (pKa=-5.6), dicinnamalacetone (pKa=-3.0), and 4-(phenylazo)diphenylamine (pKa=+1.5). The acid amount was titrated according to the Benesi method.[5]

We examined the efficiency of the SA-Mont in *meso*-tertapentylporphyrin synthesis.[1] Figure 1 shows the dependence of the porphyrin yield, the average pore diameter of the SA-Mont, and the density of acid sites of $H_0 \leq -5.4$ on the clay surface on the sulfuric acid treatment time. Although the parent Na-Mont has no activity, a gradual increase in the porphyrin yield was observed until the acid-treatment time reached 3.5 h. The montmorillonite treated with sulfuric acid for 3.5 h (abbreviated as 3.5 h-SA-Mont) has almost the same efficiency (39% yield) as K10 (46% yield). Upon the extended acid treatment for over 3.5 h, however, the yield abruptly fell, and finally became below 1% on the 8 h-acid treatment.

Concerning the acid property of the SA-Mont, the acidity[4] was $-3.0 < H_0 \leq +1.5$ for the parent Na-Mont, $H_0 \leq -8.2$ for 0.25-5 h-SA-Mont, and $-8.2 < H_0 \leq -5.6$ for 8 h-SA-Mont, respectively. Therefore, it seems likely that the acidity of $H_0 \leq -5.6$ is at least required for clay to perform the porphyrin synthesis. Figure 1 indicates that there is no apparent correlation between the acid site density in the range of $H_0 \leq -5.6$ and the porphyrin yields.

In terms of a structural interest, the SA-Mont was found to possess only mesopores with little or no micropores, judging from good agreement between their surface areas treated by the BET and t-plot methods in the N_2 adsorption isotherms.[6] The mesoporosity of the SA-Mont can be roughly evaluated by the average pore diameter which is calculated as a simple cylinder model from the surface area and adsorbed volume.[7] As shown in Figure 1, the porphyrin yield reaches the maximum value when the average pore diameter of 3.5 h-SA-Mont is nearly 13 nm, suggesting that the porphyrin yields are associated with the porosity properties rather than the acid site density of the clay. To define the porosity of clay, it is important to know the pore-size distribution. The type of hysteresis loops in N_2 adsorption-

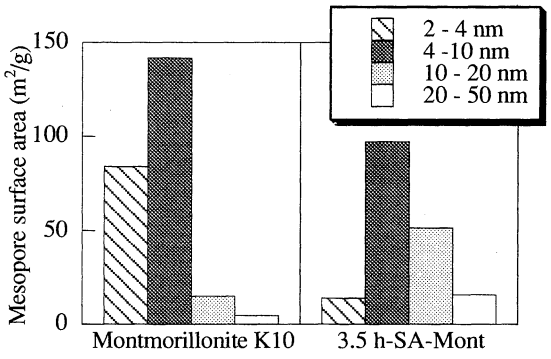
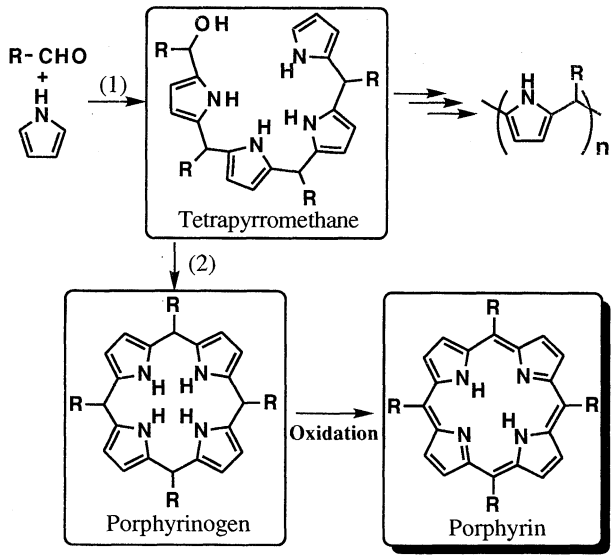


Figure 2. Mesopore-size distributions of montmorillonite K10 and 3.5 h-SA-Mont.



Scheme 1. The formation of *meso*-substituted porphyrin from aldehyde and pyrrole.

desorption isotherms of K10 and 3.5 h-SA-Mont belongs to H1-type[7] because there is no sharp dip in the desorption isotherm at relative pressures of around 0.5. The pore-size distributions were obtained by using a cylindrical pore model (the BJH method[8]) as shown in Figure 2, indicating that K10 and 3.5 h-SA-Mont have mesopores mainly ranging 4 to 10 nm in diameter. The dimension of *meso*-tertapentylporphyrin is approximately 2.0 nm in diameter. Therefore, it is reasonable to presume that the mesopores of K10 and 3.5 h-SA-Mont function as effective reaction media for the porphyrin formation.

The formation of *meso*-substituted porphyrin from aldehyde and pyrrole proceeds through two main stages as shown in Scheme 1: (1) cooligomerization of aldehyde and pyrrole to form tetrapyrromethane, and (2) cyclization of the tetrapyrromethane to give a cyclic porphyrinogen, followed by oxidation to porphyrin. The first stage is influenced by the concentrations of the reactants.[1,2] In the second stage, the cyclization step inevitably competes with the formation of longer linear copolymers, leading to low efficiency in the porphyrin synthesis. It is expected that in the mesopores of K10 and 3.5 h-SA-Mont, the longer linear copolymer formation is less promoted, and that the intramolecular cyclization is more accelerated, resulting in efficient production of porphyrins, compared with the porphyrin synthesis under homogeneous conditions.

To make the effect of mesopores in porphyrin synthesis much clearer, we applied newly developed FSM-16[9] containing alumina, which has homogeneous mesopores, to the *meso*-tetraalkylporphyrin synthesis. We employed three kinds of FSM-16 (including 4 wt% of Al_2O_3) bearing different pore sizes of 2.0, 2.8, 3.4 nm in diameter in the *meso*-tertapentylporphyrin synthesis. The three FSM-16 were found to have almost the same acid site density, $(24\pm5)\times10^{-5}$ mmol/m^2, in the range of $H_0 \leq -5.6$, and the difference in the pore size directly reflected porphyrin yields: the mesopores of 2.0 nm was impractical (in less than 1% yield); FSM-16 with mesopores of 2.8 nm gave the highest yield (27%); and by using larger pores of 3.4 nm, the porphyrin yield was down to 17%. These results strongly support the idea that pores in a certain nanometer range can work as efficient templates for macrocycle formations from linear precursors.

The mesopore structure of FSM-16 is honeycomb-like, and is entirely different from that of SA-Mont. Therefore, we can not assert the suitable size of mesopores for the porphyrin synthesis, simply comparing the results between K10, SA-Mont, and FSM-16.

In conclusion, a great increase in the porphyrin yield is taken account for by the presence of mesopores in K10 and SA-Monts where polymerization-cyclization steps to form porphyrinogen are highly promoted. In the accompanying paper, we will propose the models of mesopores in K10 and SA-Mont.

We thank Mr. Sinji Inagaki of Toyota Central R & D Labs for a kind gift of FSM-16.

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