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Hierarchical design of mixed metal oxides: novel macroporous VPO phases

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Macroporous vanadium–phosphorus–oxide phases (macro-VPO) displaying ordered 0.2–0.4 μm pores and unprecedented high surface areas (44–75 m^2 g^{-1}) have been synthesized using colloidal arrays of polystyrene spheres as a template.

Mixed metal oxides possess promising catalytic properties for the selective oxidation of lower alkanes (C_2–C_5).[1] For example, Mo–V–Nb and Sb–V oxides are catalytically active in selective oxidation of ethane and propane[2] and propane ammoxidation and vanadium–phosphorus–oxides (VPOs) are selective in the oxidation of *n*-butane to maleic anhydride.[3]

The conventional synthesis methods, both wet chemistry and solid-state, offer limited control over the phase, bulk and surface compositions of mixed metal oxides, preferential exposure of active and selective surface planes, surface areas and pore architectures, which define their catalytic properties in selective oxidation of lower alkanes. There is a critical need for novel routes of assembling hierarchically designed mixed metal oxides, which display remarkable ordering on micro- (< 3 nm for the surface region structure and composition), nano- (3–100 nm for the bulk and phase compositions) and macro- (> 100 nm for pore architectures) scales.

Macroscale-templated synthesis of nanocrystalline mixed metal oxides represents an attractive approach for the synthesis of hierarchically designed catalytic materials. Several single-element macroporous oxides with very interesting structural properties have been synthesized by self-assembly using colloidal sphere templates.[4–9] However, macroporous mixed metal oxides for applications in oxidation catalysis have not, as yet, been reported. We report here the first successful example of a hierarchically designed macroporous mixed vanadium–phosphorus–oxide (macro-VPO) with desirable structural and compositional properties for selective oxidation of *n*-butane.

Macro-VPO phases were assembled using close-packed arrays of colloidal polystyrene (PS) spheres (0.4 μm diameter) as a template. Monodispersed PS spheres were synthesized by an emulsion polymerization process described elsewhere.[7] The ordered arrays of PS spheres were obtained by either centrifugation or filtration of PS sphere suspensions. Fig. 1 shows the SEM image (Hitachi, Model S-3200N) of colloidal PS spheres used as the template.

In a typical synthesis, an array of PS spheres was first impregnated with a phosphoric or phosphorous acid solution in ethanol. Then a solution of a vanadium-(IV) or -(V) source in ethanol or isobutyl alcohol was introduced into the voids of the array, where it reacted with a phosphorus source and condensed into a macro-VPO framework upon drying. It was found that the initial surface treatment with a phosphorus source was critical for the nucleation and growth of macro-VPO phases in the voids of the PS sphere arrays. In all experiments the P/V molar ratio was 1 : 1, which provides the optimal surface and bulk composition for selective oxidation of *n*-butane.[3] The PS spheres were removed from as-synthesized macro-VPO by either calcination in air at 723 K or Soxhlet extraction using a mixture of acetone and tetrahydrofuran (1:1 volume ratio). Typical synthesis conditions, crystallographic phases determined by powder XRD (Siemens D-500) and the BET surface areas (Micromeritics Gemini 2360) for selected calcined and Soxhlet-extracted macro-VPO phases are given in Table 1.

The ordered pore structure of the macro-VPO phases after the template removal is evident in Fig. 2. Interconnected pores appear as dark spots (*ca.* 0.2 μm diameter) inside spherical 0.4 μm cavities left after the removal of the PS spheres. The walls of the macropore structure are formed by the $(VO)_2P_2O_7$ nanocrystals. The wall thickness was estimated from the SEM images to be *ca.* 90 nm. The average nanocrystal size determined using the Scherrer formula[10] was *ca.* 20 nm, which indicated that the wall was only four crystals thick. Relatively large size of the nanocrystal building blocks explains the

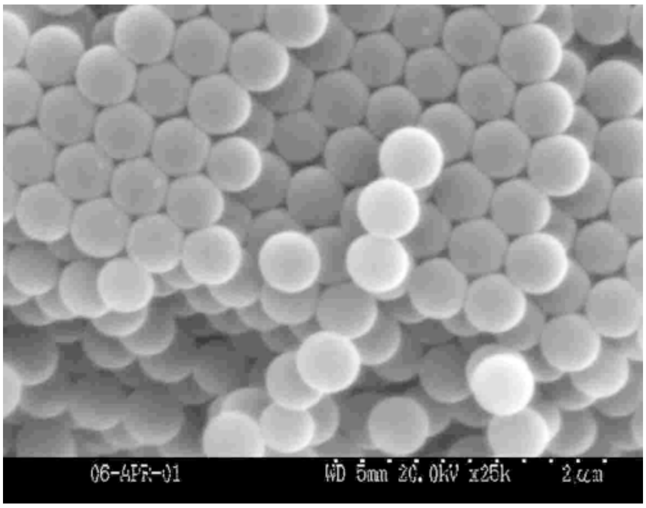

Fig. 1 SEM image of the synthesized monodispersed polystyrene spheres used as templates for the formation of macroporous VPO.

Table 1 Selected properties of macroporous VPOs

VPO sources	General description	Specific surface area/m^2 g^{-1}	Crystalline phase
$VO[CHO(CH_3)_2]_3$, H_3PO_3	Calcined in air at 723 K	64	$VOPO_4 \cdot 2H_2O$
$VO[CHO(CH_3)_2]_3$, H_3PO_3	Soxhlet extracted	50	$VOPO_4 \cdot 2H_2O$
V_2O_5, H_3PO_3	Calcined in air at 723 K	41	$VOPO_4 \cdot 2H_2O$
V_2O_5, H_3PO_3	Soxhlet extracted	75	$VOHPO_4 \cdot 4H_2O$/β-$VOHPO_4 \cdot 2H_2O$
V_2O_5, H_3PO_4	Calcined in air at 723 K	44	$(VO)_2P_2O_7$

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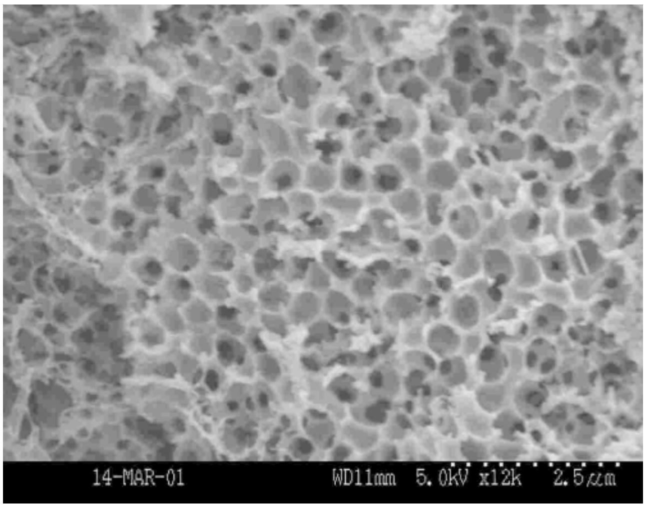

Fig. 2 SEM image for macroporous VPO.

somewhat rough and disordered appearance of the macropore structure in SEM images (Fig. 2).

The macroscale-templated synthesis produced the VPO phases with unprecedented high surface areas after the removal of the PS spheres. The macro-VPO phases displayed *ca.* 44–75 $m^2 g^{-1}$ surface areas (Table 1) and the optimal bulk compositions (P/V *ca.* 1.05 by ICP elemental analysis). By comparison, the surface areas of VPO phases synthesized by conventional methods are in the range 5–20 $m^2 g^{-1}$.[1,3] The surface areas of the macro-VPO phases are consistent with a theoretical estimate for 20 nm cubic crystals of $(VO)_2P_2O_7$ (90 $m^2 g^{-1}$).

The present method of macroscale-templated synthesis of mixed metal oxides yielded $(VO)_2P_2O_7$ which preferentially exposed the active and selective surface (100) planes for the oxidation of *n*-butane. $(VO)_2P_2O_7$, which is the active and selective phase in *n*-butane oxidation to maleic anhydride,[1,3] was synthesized using the V(IV) and P(III) sources (Table 1). The intensity ratio of the interplanar (100) and in-plane (042) X-ray reflections of $(VO)_2P_2O_7$ (I_{100}/I_{042}) has been previously used to determine the prefential exposure and the stacking order of the surface (100) planes proposed to contain the active and selective catalytic sites.[3] The conventional VPO phases typically exhibited low intensity ratios, I_{100}/I_{042} *ca.* 0.4, indicating that the surface (100) planes were not dominant in these phases.[3] The macro-VPO phases are characterized by much higher intensity ratios, I_{100}/I_{042} *ca.* 2.48 suggesting that these phases preferentially expose the surface (100) planes of $(VO)_2P_2O_7$.

To the best of our knowledge, the hierarchical design of the mixed metal oxide phases with ordered macropore architectures, record high surface areas, as well as the phase compositions and the surface plane exposures critical for selective oxidation catalysis is achieved for the first time. This study demonstrated that the macroscale self-assembly route holds a great promise as a general method for the rational design of mixed metal oxides with desirable structural and compositional properties.

Further studies will focus on the catalytic performance of the novel macroporous mixed metal oxides in the oxidation of lower alkanes.

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