

Nanostructural Control of Catalytic Activity

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Introduction

We have recently developed a novel synthetic route based on chemical reactions in aerosol droplets to form nanostructured mixed metal oxides for epoxidation catalysis.^{1,3} The materials are silica/titania mixed oxides with a moderately low content of titania (about 20 to 25% Ti/Si by ICP). In experiments done at the APS on the UNI-CAT beamline (33-ID), we examined a series of samples with a close to constant Ti/Si molar ratio. The powders showed variable catalytic activity in an epoxidation reaction of cyclohexene with cumene hydroperoxide. The reactivities varied from about 8% conversion to 0% conversion. These are rather low conversions, but no extraordinary care was taken to remove water or oxygen from the reaction mixture since one of the goals of the work is to produce heterogeneous catalysts that are not sensitive to water and oxygen contamination. Prior to the APS measurements, we also knew that the catalytic activity was reduced when the powders were baked under mild conditions of 140°C under vacuum for 24 hours. We believed that this was due to the removal of organic groups from the catalytic surface. Organic groups might enhance catalytic activity by creating a hydrophobic catalyst interface, water being detrimental to the epoxidation reaction.

From a structural perspective, we were interested in demonstrating that catalytic activity could be enhanced in small particles. A demonstration of control over catalytic activity through manipulation of nanostructure was one of the main results of this study. We anticipated this result from observed shifts in the UV absorption pattern as a function of particle size in a previous study.

Methods and Materials

Nanostructured mixed oxides were used as prepared and after baking under vacuum for 24 hours at 140°C. The dry powders were sprinkled on scotch tape in as close to a thin monolayer as was possible. The specific surface area of the powders was approximately 800 m²/g. All powders contained a molar ratio of Ti to Si of about 20 to 25% based on Ti and Si species. The powders were used as heterogeneous catalysts in an epoxidation reaction of cyclohexene with cumene hydroperoxide. The conversion ratio to cyclohexene epoxide is given in Table 1 for the powders reported here.

Results

Figure 1 shows ultra-small angle x-ray scattering (USAXS) data taken on the UNI-CAT ultra-small-angle camera for the series of four mixed oxide heterogeneous catalysts. The two samples, 57A and 53B, show similar primary particle structure (high-q) but different aggregate structure (intermediate-q). Catalyst 57B shows much larger primary particle structure (low-q), while 77A does not display primary particle structure in the size scales

Sample	Conversion %	R _{g1} , Å	R _{g2} , Å	d _f
57A	8.35	33.0±0.4	188±10	2.37±0.02
53B	4	32.1±0.4	613±23	2.09±0.01
57B	1.3	757±17	1.4µm±0.8	1.62±0.09
77A	0	>3µm	--	--
57A Baked	6.7	17.2±0.3	505±33	2.02±0.01
53B Baked	1.9	26.2±0.8	181±100	2.1±0.5
57B Baked	2.5	659±9	2.4µm±2	1.78±0.03
77A Baked	0	>3µm	--	--

Table 1. Catalyst fit results and epoxidation conversion.

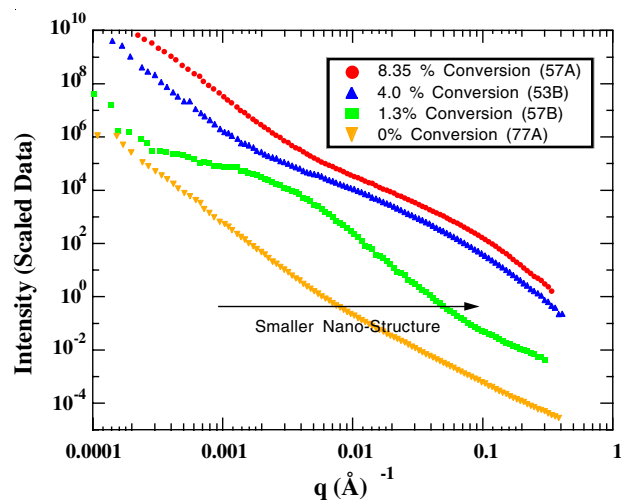


FIG. 1. USAXS data show smaller nanostructured catalysts with enhanced reactivity.

probed by the USAXS camera, 10 to 10,000 Å. The data were fit using the unified function,^{4,6} and two of the fits are shown in Fig. 2, which compares baked and unbaked samples.

The unified fit of Fig. 2 includes four free parameters under a mass-fractal/spherical primary particle model as described in reference 4. The baked sample shows a reduction in the primary particle size that may be associated with removal of organic groups from the primary particles. Removal of organic groups could lead to a diminished catalytic activity due to increased hydrophilicity of the active sites. In addition to reduction in the primary particle size, the mass-fractal aggregates grow and the mass-fractal dimension decreases. This could also result from removal of organics as the primarily inorganic species in the primary particles and aggregates become more attractive to each other. Such cluster-cluster growth is known to lead to a reduced mass fractal dimension compared to monomer-cluster growth from the synthetic process.⁷

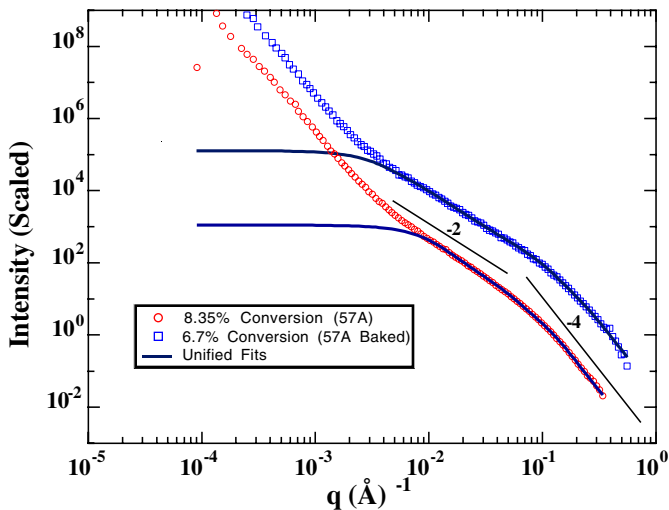


FIG. 2. Unified fit to sample 57A and baked 57A. The baked sample shows reduction in primary particle size and growth of aggregate structure as well as a reduction in the mass dimension.

Discussion

The preliminary results of this on-going study support a dependence of catalytic activity on both the primary and aggregate structure in these mixed oxide heterogeneous epoxidation catalysts. Additionally, the chemical composition at the catalyst surface appears to govern the reactivity. From previous studies we have evidence from IR spectroscopy for removal of organic groups under the mild conditions under which the samples were baked.^{1,3} We plan to further confirm this chemical change using IR. Previously we have reported a reduction in the specific surface area in silica nanopowders of this type on baking. The USAXS results indicate an increase in specific surface area, and this will be confirmed using nitrogen gas absorption. The results from the UNI-CAT USAXS instrument are vital to the understanding and continued development of these novel catalytic systems.

Acknowledgments

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