

## Benzylation of Aromatic Compounds with Different Crystallites of MgO

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Transition metal complex mediated homogeneous catalysts exhibit higher activity and selectivity in organic transformations due to the presence of a single active site with a defined shape and stereochemistry. Heterogeneous catalysts composed of assorted crystal structures with different shapes possess several kinds of active species, which exhibit different reactivities and usually lower activity and selectivity. This has necessitated the exploration of crystals with defined shapes in catalytic reactions in an effort to understand the reactivity versus the shape/face of the crystal. Some heterogeneous catalysis examples highlighting the importance of defined shape/face or orderly structures in enhancing activity/selectivity have been reported.<sup>1–5</sup> V<sub>2</sub>O<sub>5</sub> supported on TiO<sub>2</sub> (anatase) shows superior activity over the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (rutile) in the partial oxidation of *o*-xylene.<sup>1</sup> The active phase formed upon selective adsorption of (*R,R*)-tartaric acid on the Cu(110) face reduces ketoesters enantioselectively.<sup>2</sup> The desorption energies of (*R*)- and (*S*)-propylene oxides from Cu(643)<sup>R</sup> and -(643)<sup>S</sup> surfaces depend on the relative handedness of the adsorbate/substrate.<sup>3</sup> Ni–Al layered double hydroxides with ordered cation distribution are demonstratively superior over the other Ni–Al layered double hydroxides in the oxidation of alcohols using molecular oxygen.<sup>4</sup>

Porous nanocrystalline inorganic oxides are of topical interest, because they exhibit different characteristics in band gaps,<sup>6</sup> magnetic moments,<sup>7</sup> specific heats,<sup>8</sup> melting points,<sup>9</sup> surface chemistry,<sup>10</sup> and morphology/particle shape.<sup>11</sup> Having variable properties depending on the size of the particles, the inorganic oxides present enormous opportunities. Nanocrystalline alkaline earth inorganic oxides have been efficiently used as adsorbents for gases and destruction of hazardous chemicals, whereas the catalytic properties of these materials are seldom explored.<sup>12a,b</sup> Although solid acid mediated Friedel–Craft reactions involving electrophilic substitution of aromatic compounds have been well studied, there is only one example to our knowledge using a solid base (thallium oxide) mediated Friedel–Crafts benzylation reaction.<sup>13</sup> We report herein an unusual example where solid bases are used as the starting catalytic materials for Friedel–Crafts type alkylation.<sup>14</sup> It is demonstrated that alkaline earth metal oxide nanocrystals are effective in this chemistry. It has been possible to draw a correlation between surface area and crystal shape, and the results are surprising.

Commercial MgO [CM–MgO (SA: 30m<sup>2</sup>/g)] was purchased from Aldrich. Samples of conventionally prepared MgO [CP–MgO (SA: 250 m<sup>2</sup>/g)] and aerogel prepared MgO [AP–MgO-1 (SA: 390 m<sup>2</sup>/g), AP–MgO-2 (SA: 590 m<sup>2</sup>/g)] were synthesized as reported in the literature<sup>10b</sup> and are described in detail in the Supporting Information. Silylation of CP–MgO and AP–MgO to obtain silylated derivatives (Sil–CP–MgO and Sil–AP–MgO) is described in the Supporting Information.

Surface areas, pore volumes, and pore diameters of all materials that were studied as catalysts in the benzylation of toluene, xylenes, and benzene are depicted in Table 1, Supporting Information. Both the CP–MgO and the AP–MgO, in general, showed higher rates of benzylation of *o*-xylene over toluene, while they were essentially inert in the benzylation of benzene (Figure 1, Supporting Information). While the observed phenomenon is primarily in agreement with nucleophilicity of aromatic compounds, the effect of the reflux temperature cannot be ruled out. The activity profile of benzylation of toluene with polycrystalline CM–MgO, microcrystalline CP–MgO, and nanocrystalline AP–MgO is in the order CP–MgO > CM–MgO > AP–MgO-1 > AP–MgO-2, as is evident from Figure 1. This observed trend was surprising in that the higher surface area samples (AP–MgO) were poorer catalysts. Furthermore, similar experiments with AP–CaO versus CP–CaO showed somewhat slower kinetics but again with AP samples less reactive than CP. These results were reproduced numerous times with several preparative batches of the AP and CP samples of MgO and CaO.

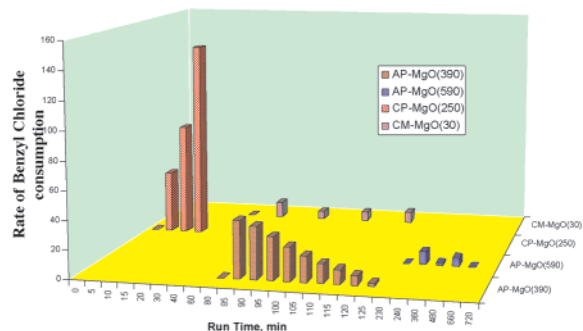
To understand these unusual phenomena, it may help to examine the shape of these oxide crystals. The CM samples are generally large cubic crystals, the CP samples are thin hexagonal platelets about 150 nm long and 10 nm thick having large exposed areas of the (100) crystal face, while the AP samples are very small, irregular stacks of square plates exhibiting numerous crystal faces, edges, and corners.<sup>11b</sup> Models<sup>11b,14,15</sup> indicate that the percentage of corner and edge sites on the surface of the AP–MgO could approach 20%, while on CP–MgO it is less than 0.5%, and on CM–MgO it is essentially 0%. If the most reactive surface sites (corners, edges, defects) were productive, the AP sample might be expected to exhibit 40-fold enhanced rates, even without considering surface areas. However, CP–MgO exhibits at least a 6-fold higher rate for toluene benzylation (Figure 1).

Before speculating about the reason for these unexpected findings, some additional data are helpful. Differential thermal analysis (DTA) of the used catalysts exhibited two endotherms in the 270–600 °C range (see Supporting Information, Figure 6). According to DTA–TGA–MS of the used catalysts, a major component given off was *m/z* = 91 corresponding to the benzyl radical cation, and the CP–MgO released a small amount at lower temperature (about 300 °C), while the AP samples released larger amounts with a large endotherm about 470 °C. No *m/z* value corresponding to the benzylation product, phenyl tolyl methane, was detected in the mass spectrum, substantiating that the 91(*m/z*) was the desorbed benzyl species from the MgO surface. It appears that the AP samples strongly adsorbed organic moieties in large amounts. This could mean that catalytic sites were simply blocked by the strongly adsorbed species. These results are well in consonance with the time evolution kinetic results with the CP–MgO and AP–MgO catalysts (Figure 1). The reactivity of the CP–MgO is increased with the progress of time, which is attributed to

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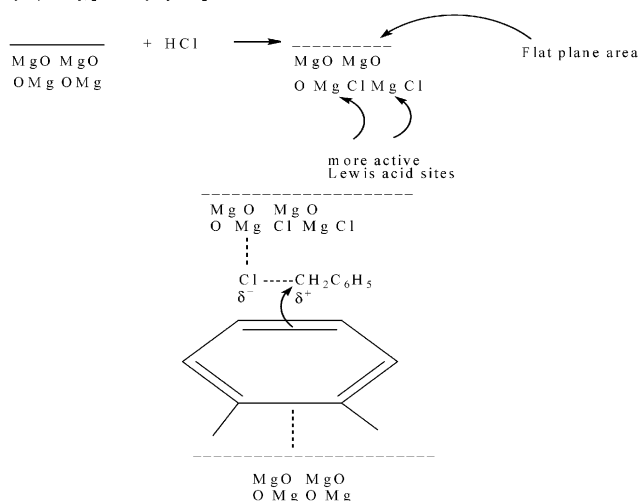
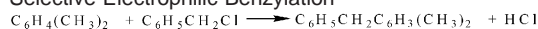
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**Figure 1.** Rates of benzylation of toluene by benzyl chloride over MgO nanocrystals. Surface areas of MgO samples are shown in parentheses. A mixture of catalyst (100 mg), benzyl chloride (6 mmol), and toluene (10 mL) was heated under reflux. All of the catalysts afforded 100% conversions and selectivities toward benzylation product, except AP-MgO(590), which shows a conversion of 85% even after 660 min. (The initial rates are AP-MgO(390) at 85 min = 40; AP-MgO(590) at 240 min = 9; CP-MgO(250) at 5 min = 44, and CM-MgO(30) at 60 min = 11  $\mu\text{mol}$  of benzyl chloride consumed/s/g of catalyst.)

**Scheme 1.** Depiction of Possible Role of MgO/MgCl Surface in Selective Electrophilic Benzylation



the increased number of active sites. Conversely, in the case of AP-MgO-1, the reaction required an induction period of 80 min to reach a certain concentration of active sites on the surface to manifest the reactivity. The activity is decreased with the progress of time due to blocking of active sites.

Powder X-ray diffraction of the used catalysts (see Supporting Information, Figure 2–4) indicated that the CM-MgO bulk phase was essentially unchanged, while CP and AP samples were almost completely converted to  $\text{MgCl}_2\text{-MgO}$  composite (which readily formed carbonates on exposure to air). Although this might seem to mitigate against any argument that crystal shape of the starting oxides is important, it is known that the conversion of 1-chlorobutane to butenes over CP- and AP-MgO samples leads to  $\text{MgCl}_2\text{-MgO}$  core/shell formation while maintaining relative structure.<sup>16</sup> This is further reinforced by the result that there was no benzylation of toluene under identical conditions for 12 h using  $\text{MgCl}_2$  as a catalyst in a control reaction. Furthermore, in the present work, the  $\text{MgCl}_2\text{-MgO}$  composite remained catalytically active when, after the reaction cycle, a fresh charge of benzyl chloride was added. Surface areas of the used catalysts, AP-MgO-1, AP-MgO-2, and CP-MgO, were 125, 103, and 85  $\text{m}^2/\text{g}$ , respectively, also suggesting that the morphologies of these crystals have not been destroyed.

Another series of experiments involved silylating the MgO samples with  $(\text{CH}_3\text{O})_3\text{SiCH}_3$  to protect surface -OH groups and

block them from participation in subsequent benzylation chemistry. Interestingly, very little change in catalytic properties was realized, which shows that surface -OH groups are not important in this context (see Supporting Information, Figure 5).

Coming back to the discussion of the main results, we have noted one other interesting feature. For toluene benzylation, the AP-MgO sample exhibited an induction period, but the CP-MgO did not (neither one exhibited an induction period with xylenes, and benzene was inert to both). This suggests that perhaps a deeper conversion to magnesium chloride is necessary before the most active catalytic sites are established.

On the basis of these results in total, we conclude that for these unusual catalysts: (1) Microcrystalline MgO can serve as a selective benzylation catalyst. (2) The pore diameter has no influence on the rate of benzylation, because the average pore diameters of CP-MgO, AP-MgO-1, and AP-MgO-2 are large enough to allow the reactants free access to the active sites and the products to diffuse out freely. (3) Active sites are due, at least in part, to  $\text{MgCl}_2$  formation ( $\text{Mg}^{2+}$  Lewis acidity is increased), and perhaps good activity can be attributed to an optimal combination of  $\text{MgCl}_2/\text{MgO}$  edge and plane sites, Scheme 1.<sup>17</sup> (4) Shape and exposed crystal faces are important in allowing appropriate adsorption, molecular trafficking, and desorption energies, and perhaps the  $\text{MgO}(100)$  face is particularly important in this regard, because the CP-MgO hexagonal crystals expose the most (100) face surface.

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**Supporting Information Available:** Preparation and characterization of catalysts, experimental procedure for benzylation of toluene, *o*-xylene, and benzene, and reaction kinetics (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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