

# STUDY ON NITROGEN SORPTION DATA FOR ORGANOSILANES GRAFTED ONTO ZEOLITE Y

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## INTRODUCTION

The oxidation of R-methyl glucoside, benzyl alcohol, and 1,4-pentanediol were catalyzed by the TEMPO hybrids in aqueous solution.<sup>39</sup> The R-methyl glucoside was oxidized to 1-O-methyl glucuronate at 0 °C with NaOCl, giving almost 100% conversion within 30 min for both the ether- and amide-TEMPO- MCM-41 catalysts. The selectivity was over 95% to the carboxylic acid product. No leaching of the TEMPO groups was observed. The catalysts were also useful in the reaction of benzyl alcohol with oxygen and copper (I) chloride in DMF. Conversion over the ether-TEMPO-MCM-41 was 35%, and selectivity to benzaldehyde was 99%. Under similar conditions, the homogeneous TEMPO gave 94% conversion and 99% selectivity. The small amount of water present in the reaction media prevented the over oxidation to benzoic acid. The lower activity of the supported TEMPO is reasonable because the proposed mechanism of the reaction requires two adjacent TEMPO molecules to be involved in a disproportionation step. The organic loading in the MCM-41 material was not sufficient to have a significant number of TEMPO moieties in close proximity to each other. Oxidation of the 1, 4-pentanediol to  $\gamma$ -valerolactone was also catalyzed by the TEMPO-containing hybrid solids, giving 50% conversion with over 95% selectivity. The amide-TEMPO-MCM-41 was treated with hydrogen bromide prior to reaction to transform unreacted aminopropyl groups into ammonium bromides. Prior work has shown that the presence of these ammonium species can improve catalytic activity in the diol oxidation. As expected, the HBr-treated amide- TEMPO-MCM-41 was more active than the untreated material and gave 99% conversion with over 95% selectivity under conditions similar to those of the ether-linked TEMPO.

Chiral functionalities can also be grafted into silicas through similar techniques as described above. Brunel and co-workers have introduced chirality into mesoporous silicas via the grafting method.<sup>40-45</sup> The chiral hybrid catalysts were then used to perform enantioselective reactions. Bellocq et al. described the immobilization of the chiral amino-alcohol (-)- ephedrine on MCM-41-type silicas via nucleophilic modification of the halopropyl groups.<sup>40</sup> Reaction of a chloropropylsilane with ephedrine yielded the desired ephedrine organosilane, but cyclization of the silane also occurred by replacement of the alkoxy groups on silicon with the hydroxyl group of the ephedrine (Scheme 24). A cleaner reaction was possible when the substitution occurred after grafting of the (chloropropyl) silane onto the MCM-41 solids.

## Material and method:

Chloropropyl group loadings on the mesoporous materials were 1.2-1.4 mmol/g, only 58-76% of these were displaced by ephedrine. The ephedrine loadings ranged from 0.83 to 0.88 mmol/g. Similar grafting of amorphous silica had lower overall functional group loadings (due to lower density of surface silanol groups) of 0.5-0.9 mmol/g of chloropropyl moieties. However, a higher percentage of 60-84% of the chloropropyl moieties tethered on amorphous silica was displaced by ephedrine during modification, giving 0.44-0.53 mmol/g of ephedrine. Bellocq et al. concluded that the greater steric hindrance in the mesopores of MCM-41, compared to amorphous silica, hindered the nucleophilic attack by ephedrine.

The ephedrine hybrids were then used in enantioselective addition reactions (Scheme 25). Amorphous silica hybrids produced high selectivities to the 1-phenylpropan-1-ol of 80-85% but had low enantiomeric excess (ee) of 11-22%. The MCM-41 hybrids also gave 84-87% selectivity but had 37% ee. Bellocq et al. noted that residual alkoxy groups on the functionalized MCM-41 surface for the organosilane grafting needed to be hydrolyzed by NaHCO<sub>3</sub> in methanol prior to addition of the ephedrine to prevent the cyclization products (as described above).

Removal of the residual alkoxy groups improved the selectivity to 91% with an ee of 40%. Further work improved the surface coverage of organic groups by utilizing a sol-gel method of functionalizing aluminosilicate mesoporous materials, Al-MTS. The Al-MTS materials were exposed to (chloropropyl) silane in toluene in the presence of water and NH<sub>4</sub>F-pTsOH. The chloropropyl moiety loadings were increased from 2.1 mmol/g via traditional anhydrous conditions to 4.4 mmol/g by the new tethering procedure. Modification by (-)-ephedrine then resulted in increased loadings of 1.9 mmol/g for chloropropyl-containing Al-MTS prepared by the new technique (as compared to 1.3 mmol/g for chloropropyl-containing Al-MTS from anhydrous methods).

The increased organic loadings greatly reduced the available void space within the materials; Al-MTS supports of larger initial pore diameters (8.3 nm instead of 3.6 nm) were then used. The catalysts were studied in enantioselective addition reactions (Scheme 25). The ephedrine-containing Al-MTS catalysts prepared by anhydrous techniques gave 93% selectivity and 47% ee, similar to the ephedrine-containing MTS silicates described above. However, the ephedrine-containing Al-MTS catalysts prepared by the sol-gel method gave 98% selectivity and 64% ee.

These results were comparable to that of the homogeneous (-)-ephedrine catalyst, which gave 98% selectivity and 65% ee. The improved activities and enantioselectivity of the ephedrine-containing Al-MTS catalyst was attributed to the higher organic coverage of the surface (preventing racemic reaction on unfunctionalized surfaces) and the larger initial pore diameter, which allowed for increased accessibility to the active sites on the support.

Lasperas et al. compared the (+)-ephedrine-modified MCM-41 materials to (-)-ephedrine.<sup>42</sup> As previously discussed, the (-)-ephedrine MCM-41 hybrid gave 37% ee to the (*R*)-isomer at conversions of 89-99% with selectivities of 84-89% to the secondary alcohol. The (+)-ephedrine hybrid yielded the (*S*)-1-phenylpropan-1-ol, in 26% ee, with similar conversions and selectivities. This suggests that the heterogeneous, chiral solids conform to the asymmetric induction observed in homogeneous chiral catalysts.

Recently, Kim et al. reported the anchoring of a proline derivative onto mesoporous silicas for use as catalysts in the preparation of chiral secondary alcohols.<sup>46</sup> The proline moiety was incorporated by modification of grafted chloropropyl species on amorphous silica, MCM-41 and SBA-15. The surface silanol groups were passivated by hexamethyldisiloxane (HMDS) after grafting of the chloropropyl silane to prevent sites for racemization to occur. The mesostructures of both MCM-41 and SBA-15 were stable throughout the modification procedure as observed by XRD. Nitrogen adsorption data showed that the MCM-41 samples had pore diameters of 23-24 Å; the SBA samples had diameters around 85 Å. <sup>13</sup>C CP/MAS NMR confirmed the integrity of the proline functional groups after grafting and modification.

The catalytic properties of these hybrids were tested in the asymmetric addition of diethylzinc to benzaldehyde in the presence of *n*-BuLi. The analogous homogeneous reaction system resulted in 87% yield with 93% ee. Grafting of the proline onto amorphous silica gave 41% ee at only 69% yield.

Passivation of the surface with HMDS after grafting slightly improved results (43% ee and 74% yield). The MCM-41 hybrids showed better results of 84 and 96% yield (not passivated and passivated, respectively) and ee's (26 and 64%). SBA hybrids were the best catalysts of all, with 52 and 75% ee and 97 and 98% yield for not passivated and passivated surfaces, respectively. The grafting of various organic moieties onto zeolites has been reported. In general, modification of zeolites by organosilanes has been used to passivate the silanol groups on the external surface or to adjust the pore diameter. Brunel and co-workers functionalized zeolite Y (calcined and dealuminated) of various Si/Al ratios with (3-chloropropyl)trimethoxysilane (CPS) and (3-aminopropyl)triethoxysilane (APS) to study the influence of the Al sites and pore size on the grafting.<sup>47</sup> Modification of the amine-functionalized zeolites was then performed by the addition of 4-anisoyl chloride and 2,3-butanedione. The samples were characterized by elemental analyses, IR, <sup>13</sup>C MAS NMR, adsorption, XRD, and TGA.

The micropore volume of the zeolite Y solid decreased substantially by one-third or more after functionalization (Table 3).<sup>47</sup> Subsequent modification of the amine groups further reduced the pore volume. Organic loadings were 0.97-1.48 mmol/g, as determined by TGA. Modification of the amino groups appeared to occur on about half of the amines (organic loadings of 0.46-0.61 mmol/g; however, the elemental analyses were inconsistent with the TGA data). Comparisons of available external and internal surface areas of the solid, before and after treatments, suggest that

most of the functionalization occurs on the external surface and at the pore mouths of the zeolite. Diffusion limitations of the organosilanes and the high reactivity of the silanes likely produce reaction at the silanol functional groups around the openings of the pores and prevent penetration within the crystal. Most of the micropores and inner cavities of the zeolite would then be blocked by the deposited organosilane. Brunel et al. pointed out that larger, sterically hindered functional groups are much more easily grafted and are more accessible catalytic sites for mesoporous materials than in zeolites.<sup>48</sup> Functionalization on the external surface of the zeolite eliminates shape selectivity and nullifies some of the motivation behind using zeolites in catalysis.

**Table 2.2 Nitrogen Sorption Data for Organosilanes Grafted onto Zeolite Y**

support (Si/Al ratio)	surf area(m <sup>2</sup> /g)	external and mesopore surf area (m <sup>2</sup> /g)	Micropore vol (cm <sup>3</sup> /g)
unmodified HY (2.5)	751	48	0.31
chloropropyl Y (2.5)	417	33	0.17
aminopropyl Y (2.5)	479	37	0.19
unmodified HY (8)	720	126	0.26
chloropropyl Y (8)	447	90	0.16
aminopropyl Y (8)	422	92	0.15
Anisoyl,N Y (8)	382	84	0.13
Unmodified HY (17.5)	795	135	0.29
chloropropyl Y(17.5)	537	91	0.20
aminopropyl Y(17.5)	523	92	0.19
Anisoyl,N Y (17.5)	431	83	0.15

Although grafting of organosilanes onto surfaces through hydroxyl groups is a well-studied and an often used method of forming organic-inorganic hybrid materials, the tethering is done by covalently attaching the organosilane to a surface silicon atom through the silicon (surface)-oxygen-silicon (external)-carbon bond in the organosilane (Scheme 2).

The silicon-oxygen bond is then external to the surface and can be cleaved at conditions encountered in some catalytic reactions.<sup>4</sup> Obviously, if this occurs, the solids will not be able to function as recyclable catalysts. It would be desirable to have the carbon bound directly to a silicon atom on the surface. By incorporation of the organosilane into the synthesis mixture during the formation of the solid, the functional group presents itself on the surface and the silicon in the silicon-carbon bond in the organosilane is on the surface of the material (Scheme 26). This forms a more uniform dispersion throughout the solid. In this “one-pot” method, the organosilanes are co-hydrolyzed and condensed with other silica reagents, e.g., tetraalkoxysilanes, water, and the appropriate organizing molecules (used for the synthesis of ordered, mesoporous materials and zeolites), to create the synthesis mixture. Issues of importance when selecting the preparation conditions include the solubility of the organosilane in the mixture, stability of the organic functional group under reaction conditions (pH, temperature), ease of organizing molecule (structure directing agent, SDA) extraction (for ordered, mesoporous materials and zeolites), and stability of the organic functional group during the extraction process. High loadings of functional groups (up to 3 mmol/g catalyst) can be obtained by cocondensation.

## CONCLUSION

To have a useful catalyst after synthesis, one must be able to extract the organizing molecules (Scheme 26) from within the pores to create porosity; calcining the material would destroy the incorporated functional groups. Extraction techniques have been developed for both mesoporous and microporous materials.<sup>49-53</sup> Extraction of the SDA can be most effectively accomplished by acidic methanol solutions.<sup>37</sup> Ordered, mesoporous materials can be designed with specific pore sizes on the basis of the SDA and organic functionality used, but there is a lower limit to the pore size (ca. 15-20 Å). Several reviews concerning advances in co-condensation of mesoporous hybrid materials have been published.<sup>5,9,54</sup> Mann and co-workers reported the first incorporation of organic groups into mesoporous materials by co-condensation methods.<sup>55</sup> Phenyl and *n*-octyl functionalities were incorporated into MCM-41 silica by the “one-pot” method using TEOS as the silica source and hexadecyltrimethylammonium bromide (C16TMABr) as the SDA. The SDA was extracted in acidified ethanol at 75 °C for 24 h. The structure of the phenyl-MCM-41 material was preserved throughout the extraction as observed by XRD. Octyl-MCM-41 was less stable to the extraction process than the phenyl-MCM-41.

The mole percent of organosilane was varied to determine its effect on the assembly of MCM-41. Phenyl-functionalized MCM-41 was prepared with concentrations as high as 20 mol %, while the *n*-octyl-functionalized material remained high quality for up to 10% organosilane.

TEM images of the materials confirmed the hexagonal structure, and nitrogen sorption data showed a decrease in pore size from 30 Å for all-silica MCM-41 to 24 and 18 Å for the 10 and 20% phenyl-MCM-41 materials, respectively.

This work showed the possibility of directly tethering an organic functionality to the walls of the ordered mesoporous silicate (organic groups and the presence of Si-C bond confirmed by IR and NMR studies). Slade and co-workers later showed that the addition of swelling agents, such as mesitylene, could be used in the phenyl-MCM-41 synthesis to increase the pore size of the material to around 30-40 Å.<sup>56</sup> Mann et al. synthesized MCM-41 materials with other functional groups such as mercaptopropyl, amine, epoxide, imidazole, and allyl.<sup>49</sup> MCM-41 silicas were prepared by using various organosilanes and C16TMABr as the SDA at conditions of basic pH.