

# SYNLETT Spotlight 81

## Clay Catalysts in Organic Synthesis

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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### Introduction

Clay minerals are made up of layered silicates. They are crystalline materials of very fine particle size ranging from 150 to less than 1 micron. There are two basic building blocks – tetrahedral and octahedral layers, which are common to clay minerals.<sup>1</sup>

A variety of organic reactions that are catalysed by Brønsted acids such as H<sub>2</sub>SO<sub>4</sub>, HCl, and other protonic acids or Lewis acids such as AlCl<sub>3</sub>, FeCl<sub>3</sub>, etc. have been shown to

take place in clays, especially montmorillonite, more efficiently, i.e., under milder conditions, with greater selectivity, better yields, shorter reaction times and so on. The range of reactions that have been successfully performed on clay catalysts includes addition, dehydration, elimination, oxidation, rearrangement reactions, substitution, etc.<sup>2</sup>

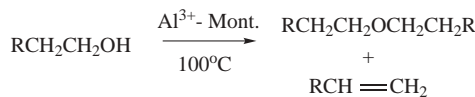
### Preparation of Clay Catalysts

Methods of cation exchange and the subsequent washing steps to remove excess salt are also well known for clays.<sup>3</sup> Between the layers of a smectite, large cationic species can be inserted by cation exchange.<sup>4,5</sup> Such bulky species act as pillars, propping apart the layers. Clayfen and clay-cop are simply prepared by evaporating acetone solutions

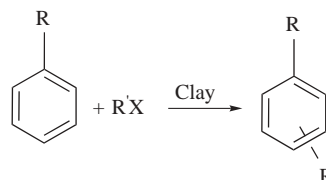
of the nitrate salts onto the clay.<sup>6,7</sup> Clayzic,<sup>8</sup> clay-supported potassium permanganate,<sup>9</sup> quaternary ammonium salts-exchanged montmorillonite,<sup>10</sup> clay-surfactants composites<sup>11</sup> and organo-clay assemblies<sup>12</sup> have also been reported.

### Abstracts

(A) The intramolecular dehydrogenation of alcohols is efficiently catalysed by both Al<sup>3+</sup>- as well as H<sup>+</sup>-exchange clays.<sup>13</sup> Primary alcohols afford mainly dialkyl ethers with little alkene production whereas secondary and tertiary alcohols provide alkenes almost exclusively.



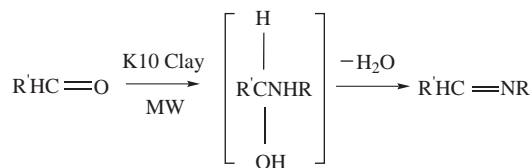
(B) Montmorillonite supported transition metal salts (zinc and nickel chlorides) are highly active and selective agents for the catalysis of Friedel–Crafts alkylation.<sup>14,15</sup>



(C) Bosch et al.<sup>16</sup> have accomplished the Beckmann rearrangement of ketoximes with montmorillonite K10 clay in 'dry' media in good yields.



(D) To develop environmentally benign synthetic protocols utilising microwave irradiation under solvent-free conditions, a simple synthetic procedure has been developed that is catalysed by montmorillonite K10 clay<sup>17</sup> for the preparation of imines and enamines.<sup>18</sup>



## References

- (1) McCabe, R. W. In *Inorganic Materials*; Bruce, D. W.; O'Hare, D., Eds.; John Wiley & Sons: Chichester, **1992**, 295.
- (2) Varma, R. S. *Tetrahedron* **2002**, *58*, 1235; and references cited therein.
- (3) Adams, J. M.; Clement, D. E.; Graham, S. H. *Clays Clay Miner.* **1983**, *31*, 129.
- (4) Corma, A. *Chem. Rev.* **1994**, *97*, 2373.
- (5) Pinnavia, T. J. In *Chemical Reactions in Organic and Inorganic Constrained Systems*; Setton, R., Ed.; Kluwer: Dordrecht, **1986**, 151.
- (6) Cornelis, A.; Laszlo, P. *Synthesis* **1980**, 849.
- (7) Cornelis, A.; Herze, P. Y.; Laszlo, P. *Tetrahedron Lett.* **1982**, *23*, 5035.
- (8) Barlow, S. J.; Clark, J. H.; Darby, M. R.; Kybett, A. P.; Landon, P.; Marhn, K. J. *J. Chem. Res., Synop* **1991**, 74.
- (9) Lee, D. G.; Noureldin, N. A. *Tetrahedron Lett.* **1981**, *22*, 4889.
- (10) Cornelis, A.; Laszlo, P. *Synthesis* **1982**, 162.
- (11) Lin, C. L.; Pinnavia, T. J. *Chem. Mater.* **1991**, *3*, 213.
- (12) Varma, R. S.; Pitchumani, K.; Naicker, K. P. *Green Chem.* **1999**, *1*, 95.
- (13) Ballantine, J. A.; Davies, M.; Patel, I.; Rayanakorn, M.; Williams, K. J.; Purnell, J. H.; Thomas, J. M. *J. Mol. Catal.* **1984**, *26*, 37.
- (14) Laszlo, P.; Mathy, A. *Helv. Chim. Acta* **1987**, *71*, 557.
- (15) Clark, J. H.; Kybett, A. P.; Barlow, S. J.; Macquarrie, D. J.; Landon, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1353.
- (16) Bosch, A. I.; de la Cruz, P.; Diez-Barra, E.; Loupy, A.; Langa, F. *Synlett* **1995**, 1259.
- (17) Dewan, S. K.; Varma, U.; Malik, S. D. *J. Chem. Res., Synop* **1995**, 25.
- (18) Varma, R. S.; Dahiya, R.; Kumar, S. *Tetrahedron Lett.* **1997**, *38*, 2039.