Catalytic Oxidations of Natural Terpenes by Environmentally Friendly Oxidants

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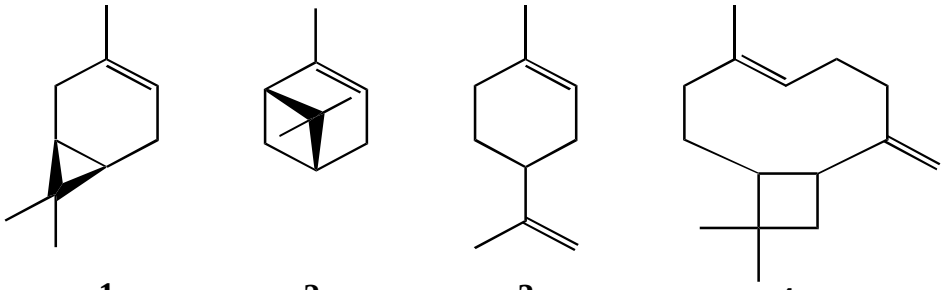
One of the challenging goal of organic synthesis and catalysis is to develop stable heterogeneous catalysts capable to operate at ambient conditions producing selectivity as high as that of homogeneous catalysts. A promising approach to designing such catalysts is to incorporate transition metal ions into the framework of mesoporous molecular sieves (MMS), which attract much attention due to high surface area and large regular pore size [1,2]. Here we report the catalytic properties of M-MMS (39 Å) with M=Co(II), Mn(II), Ti(IV) and V(V) in oxidation of various alkenes, including a number of natural terpenes (3-carene **1**, α-pinene **2**, dipentene **3**, caryophyllene **4**, etc.), by cheap and environmentally friendly oxidants, such as molecular oxygen (in the presence of iso-butyraldehyde (IBA) as reductant), *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide.

We have found that using O_2/IBA/M-MMS (M=Co(II), Mn(II) and V(V)) catalytic systems olefins of different structures can be converted to the corresponding epoxides with good-to-high selectivity (85-99%) at complete alkene conversion under mild reaction conditions (room temperature, atmospheric air pressure). Co-MMS appeared to be the most active catalyst. Neither allylic oxidation nor epoxide ring cleavage occurs. Diolefins such as **3** and **4**, can give mono- or diepoxides depending on the reaction conditions.



1 **2** **3** **4**

H_2O_2 and TBHP in the presence of M-MMS (M=Ti(IV) and V(V)) oxidize terpenes to the corresponding epoxides but selectivity of epoxidation is less as compared to O_2/IBA/M-MMS systems.

The effect of solvent nature on the M-MMS catalysts activity and stability has been investigated. Special attention was devoted to the question of leaching of active species during the oxidation processes.

References

1. R. A. Sheldon, *Stud. Surf. Sci. Catal.*, 1997, 110, 151.
2. A. Corma, *Chem. Rev.*, 1997, 2373.