EFFICIENT AEROBIC OXIDATIONS AND HYDROGEN TRANSFER REACTIONS BY SUPPORTED RUTHENIUM HYDROXIDE CATALYST

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The oxidations of alcohols and amines, and hydrogen transfer reactions such as racemization, reduction of carbonyl compounds, and isomerization of allylic alcohols are very important because their products have widely been used as various chemical intermediates. These reactions are traditionally carried out with stoichiometric metal reagents to produce enormous amounts of metal salts as wastes. In this context, the development of catalytic systems is of great importance. Herein, we report that the easily prepared supported ruthenium hydroxide catalyst $Ru(OH)_x/Al_2O_3$ is found to act as an effective heterogeneous catalyst for the aerobic oxidations of alcohols[1,2] and amines[2,3] with molecular oxygen (or air) as an sole oxidant, and hydrogen transfer reactions such as racemization, reduction of carbonyl compounds, and isomerization of allylic alcohols.[4,5]

The $Ru(OH)_x/Al_2O_3$ catalyst showed the high catalytic activities for the oxidations of activated, non-activated, heterocyclic alcohols with only 1 atm of molecular oxygen. All primary and secondary alcohols were converted into the corresponding aldehydes and ketones, respectively, in high to excellent yields. The present supported ruthenium hydroxide catalysts also showed the high catalytic activity for the oxidation of amines with molecular oxygen. All primary amines tested were converted into the corresponding nitriles in high yields. Secondary amines were oxidized to the corresponding imines. It is noted that air can be used instead of molecular oxygen in the present system without changes in reaction rate, conversions, and selectivities.

Furthermore, three kinds of hydrogen transfer reactions, namely racemization of chiral secondary alcohols, reduction of carbonyl compounds to alcohols using 2-propanol as a hydrogen donor, and isomerization of allylic alcohols to saturated ketones, could efficiently be promoted by the $Ru(OH)_x/Al_2O_3$ catalyst under unaerobic conditions. A wide variety of substrates including aromatic, aliphatic, and heterocyclic alcohols or carbonyl compounds could be converted to the

desired products in moderate to excellent yields without any additives such as bases under anaerobic conditions. A larger scale solvent-free reaction was demonstrated; the isomerization of 1-octen-3-ol with the substrate/catalyst ratio of 20000/1 showed very high turnover frequency (TOF) of 18400 h^{-1}, and the turnover number (TON) reached up to 17200.

The ruthenium hydroxide catalysts could be reusable with retention of its high catalytic performance for the above transformations. It was confirmed by ICP that the ruthenium content of the used ruthenium hydroxide catalysts were almost the same as that of the fresh catalyst and that no ruthenium was detected in the reaction solution in all cases. In addition, the reactions were completely stopped by the removal of the solid catalyst from the reaction solution. These results indicate that the observed catalysis is truly heterogeneous in nature.

References

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