DEVELOPMENT OF NANO-STRUCTURED NON-NOBLE METAL OXIDE CATALYSTS FOR APPLICATION IN 'GREEN' ORGANIC TRANSFORMATIONS

Abstract

The concept of 'sustainability' has become an important issue of the 21st century, which faces several challenges. To achieve the goal of sustainability, catalyst plays a pivotal role in most of the chemical transformations and gained extensive interest in dealing with the global challenges in academic research and industrial applications in the past century.

This work is focused on the development of non-noble metal-based oxide catalysts for industrially important 'green' organic transformations. In particular, efforts have been made to synthesize several single and double metal oxides, such as $MnWO_4$, CuO, Co-doped $MnWO_4$, and $CeVO_4$, as a new class of catalyst for different reactions. These nanostructured catalysts are prepared using the hydrothermal method. Different morphologies of the same catalysts are designed using different surfactants or templating agents to study the morphology-dependent catalytic activity. It is asserted that morphology has a significant influence on the surface properties and, in turn, on the catalytic activity of the catalyst. The prepared $MnWO_4$ catalyst is deployed for direct toluene oxidation via C−H activation to produce benzaldehyde in an acid-free mild condition. The higher surface acidity and surface charge of $MnWO_4$ nanobars give it an edge in the catalytic activity over the $MnWO_4$ nanoflowers. CuO catalyst is found to preferentially oxidise the allylic position of cyclohexene in an aerobic condition without any external oxidant. Different morphologies of CuO were prepared by varying the bases. Among them, CuO catalyst with flower-like morphology exhibits the highest catalytic activity due to its highly active {001} exposed facet. Similarly, $CeVO_4$ can oxidise the C=C position to produce benzaldehyde via the oxidation of styrene. Three different morphologies such as 'particle,' 'rod,' and 'bar' were obtained using different surfactant / templating agents. The 'particle' shaped catalyst shows the most promising result due to its surface properties. The previously prepared $MnWO_4$ catalyst is further modified via Co doping to enhance the catalytic activity, which can be used to synthesize imine by condensation of aldehyde and amine at room temperature and in an acid-free condition. The reaction parameters are varied in the catalytic reaction to obtain the optimal reaction condition. In all the cases, the catalysts and their surface properties are well characterized by different techniques, and their heterogeneity and recyclability are ascertained.

In summary, this thesis focuses on developing several non-noble metal oxides as an important new class of heterogeneous catalyst for several 'green' organic transformations.

Keywords: *heterogeneous catalysis, hydrothermal synthesis, doping, surface properties, C–H activation, manganese tungstate, copper oxide, cerium vanadate.*