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Transition metal oxide nanoparticles as efficient catalysts in oxidation reactions

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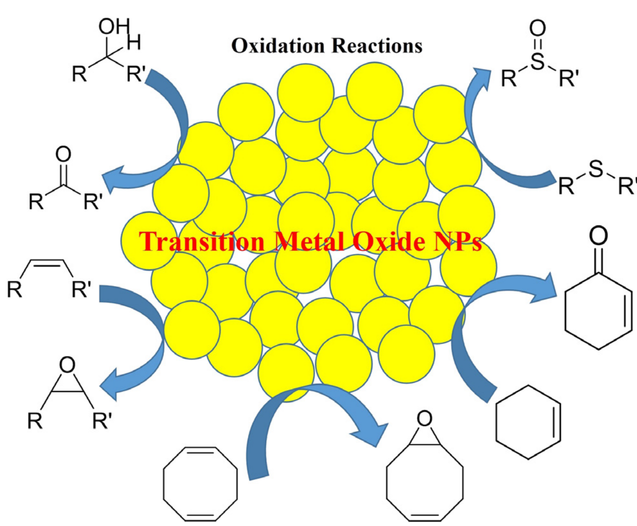
HIGHLIGHTS

- A comprehensive review of transition metal oxide nanoparticles as catalyst in oxidation reactions is presented in this article.
- This review is divided into eight main sections based on the transition metal group number.
- Different synthesis methods of transition metal oxide nanoparticles and their oxidation reaction conditions are compared and summarized.

GRAPHICAL ABSTRACT



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ABSTRACT

Studies on nano-sized particles have been the range for the past 10–15 years. With rapid growth of metal oxide nanotechnologies during the last decades, the application of this material in the field of catalysis has become a substantial research area. In the past decades, the utilization of transition metal oxide nanoparticle catalysts for industrial application in the synthesis of important chemical intermediates has been investigated by industrial and academic communities. Compared to other catalysts, one of the outstanding properties of metal oxide nanoparticles in catalysis is represented by the high selectivity which allows discrimination within chemical groups and geometrical positions, favoring high yields of the desired product. This review is devoted to dealing with the application of transition metal oxide nanoparticles as catalyst for oxidations of sulfides, alcohols, olefins, and alkanes toward the synthesis of a variety of organic compounds, such as sulfoxides, aldehydes and ketones, carboxylic acids, epoxides and alcohols.

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Contents

1. Introduction

Nowadays, oxidation reactions play a substantial role in modern chemistry as well as chemical industry. Around 30% of total production in the chemical industry is carried out by the oxidation process. It means that after polymerization, oxidation is the largest process in the production of chemicals [1–12]. On the other hand, many intermediates such as alcohols, epoxides, aldehydes, ketones and organic acids are obtained via oxidation catalysis [2–10,13–23]. From point of view of green and sustainable chemical processing, oxidation reaction has been known as an important reaction for enhancing the formation of selective products in comparison with non-selective reactions. On the other hand, in order to increase the selectivity, optimization of the catalyst process conditions are needed which satisfy the principles of green chemistry [24–27]. As a result, design and development of new catalytic oxidation processes is essential for laboratories and industries.

As an example of green oxidation, the catalytic oxidation of organic substrates to selective products has been known as one of the most important chemical transformations in organic synthesis. In this reaction, permanganate and dichromate were utilized as traditionally oxidizing reagents but they are expensive, toxic and generate to a large quantity of heavy-metal waste. Heterogeneous catalytic systems use O_2 or air as a simple and safe oxidant and produce water as the sole by-product which not only solve the above aforementioned problems but also follow the principles of green and sustainable chemical processes [28–30]. Over the last few years, considerable efforts have been devoted to the field of nanotechnology [31–36] and nano-science especially at the interface of metal and metal oxide nanoparticles (NPs) due to their relatively high chemical activity as well as specificity of interaction. These nano-sized materials in comparison to their bulk equivalents have many different properties such as a large surface-to-volume ratio [37]. Among all the materials to be prepared on the nanoscale, transition metal oxides are noteworthy candidates from a scientific as well as a technological point of view [38,39]. Transition metal oxides can exhibit unique characteristics which make them the most versatile class of materials with properties covering all aspects of solid state and materials science [40]. Oxidation reactions catalyzed by transition metal oxide NPs have recently evolved as a major research direction of our modern society resulting from an ongoing effort to miniaturize at the nanoscale processes that currently use Microsystems. Toward this end, an updated comprehensive review on transition metal oxide NPs for catalysis of oxidation reactions has not been published until now. The focus of this review is to discuss the scope and limitations of transition metal oxide NPs as an efficient catalyst for the oxidation of various organic substrates, such as olefins, alcohols, alkanes and sulfides. However the application of transition metal oxides as a support is not covered here. Consequently, this review mainly covers the literature published during the past 20 years and is divided into eight main sections based on the transition metal group number. In each section, the articles are chronologically ordered according to metal type.

2. Transition metal oxide nanoparticles

2.1. Group 4 elements (Ti, Zr and Hf)

2.1.1. Titanium oxide nanoparticles

TiO_2 NPs are well known as a photocatalyst and have been widely utilized for photochemical applications such as, degradation of organic and inorganic pollutants [41,42], solar cells [43,44], organic transformations and hydrogen production by water splitting [45]. Oxidation reactions as an important organic transformation using TiO_2 NPs have attracted much attention. In most cases, TiO_2 NPs were used as photo-degradation materials.

2.1.1.1. Alcohols oxidation. Although TiO_2 NPs have photo-degradation capacity, a significant volume of research has been recently carried out in selective oxidation of organic substrates such as alcohols, amines, aromatic alkanes and cyclohexanes by TiO_2 in the presence of O_2 under UV–Vis irradiation. For instance, a green oxidation method was developed for the oxidation of secondary alcohols to corresponding ketones by Kidwai and coworkers [46]. In this protocol, TiO_2 NPs were used as a heterogeneous catalyst in the presence of polyethylene glycol (PEG 400) as a green solvent and H_2O_2 as an oxidative regent. For the possible reaction mechanism, they proposed the production of superoxide species O^{-2} over TiO_2 NPs. As it can be seen from Fig. 1, free radicals can be formed via reaction of reactive O^{-2} with alcohols, leading to the desired products.