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Multimetallic Nanomaterial Based Catalysis

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A B S T R A C T

Nanosized material based catalysts are generally heterogeneous catalysts which have higher surface area in comparison to classical catalysts so there are enhanced catalytic activities to speed up rate of any chemical reaction or catalytic process. Nanomaterial based catalysts can be easily separated and reused with same catalytic activities. Multimetallic Nanomaterial based catalysts are drawing much attention from the chemical industry for manufacturing or synthesis of chemicals in current scenario. These Multimetallic Nano catalysts show excellent performance than their monometallic Nano catalysts. Current study of Multimetallic Nano catalysts shows that the scientists are using these catalysts (Pt-Co, Fe-Mn) in preparation of petrochemicals by Fischer-Tropsch process in which mixture of hydrogen and carbon monoxide is converted into long chain carbon compounds. These are also used to develop low temperature fuel cells. Besides this the Multimetallic Nano catalysts are also used in no. of chemical reactions from the synthetic point of view such as hydrogenation of polyenes (Ru-Sn), Selective reductive amination of nitroarens (Pd-Ag), production of hydrogen from water gas shift reaction (Pt-Au), hydrogen storage, hydrogen production via methanol (Pt-Ru, Cu-Ni) etc.

Introduction

The area of heterogeneous catalysis, with particular emphasis on catalysis involving bimetallic nanomaterials that contain two different materials in the same nanoparticle, has seen many advances over the past few years. For example, significant progress has been made with regard to the preparation and characterization of a variety of different bimetallic nanomaterials with well defined size, shape, and composition properties (Yu

et al., 2012; Cushing *et al.*, 2004; Ferrando *et al.*, 2008).

Furthermore, to allow for the development of a deeper understanding of the origins of their novel catalytic properties, extensive mechanistic studies have been directed towards heterogeneous catalysis, as summarized in several reviews (Gu *et al.*, 2012; Rodriguez, 1996).

Bimetallic nanomaterials not only combine the properties of their individual constituents but also show unique properties that are superior to those of the ordinary materials, and therefore provide an opportunity for the development of novel catalysts with enhanced activity, selectivity, and stability. The catalytic effects of bimetallic nanomaterials have been attributed to the “ligand” and “ensemble” effects of bimetallic clusters (Roucoux *et al.*, 2002; Pyykko, 2002). The ligand effect results from changes in the properties of the cluster surface that are caused by the exchange of electrons between the core metal and surface metal particles, whereas the ensemble effect is derived from the independent activation of substrates on each metal atom on the cluster surface.

Chemical reactions catalyzed by bimetallic nanomaterials

Oxidations

Oxidation reactions, especially the catalytic oxidations of hydrocarbons using molecular oxygen as an oxidant, are of considerable industrial importance (Wu and Jiang, 2012), and research towards improving the efficiency and selectivity of oxidation reactions for valuable commercial products remains a challenge. For this reason, the development of effective catalysts that can activate oxygen is highly desirable (Punniyamurthy *et al.*, 2005). Following on from the first Au cluster-catalyzed oxidation reaction reported by Haruta *et al.* (1987), there has been significant interest in Au catalysts from both the academic and industrial communities.

In this respect, Au nanomaterials are known to exhibit outstanding catalytic activity for the aerobic oxidation of alcohols (Zhang *et al.*, 2012). A variety of different Au-M (M = Cu, Pd, Pt, Ag) bimetallic nanomaterials

have recently been prepared for the selective oxidation of alcohols, where they provided significant improvements in the catalytic efficiency of this transformation.

Hydrogenations

Based on the requirements for sustainable development, as well as the desirability of using molecular hydrogen as a chemical reagent, it is of paramount importance that the chemistry community can rise to these challenges and develop highly active and selective catalysts for the hydrogenation of organic molecules, including α,β -unsaturated carbonyl compounds simple alkenes and alkynes, as well as substituted nitroarenes. Metal nanoparticles such as Ni, Pd, Ru, and Pt (Alonso *et al.*, 2011; Yan *et al.*, 2006; Xu *et al.*, 2011), have been studied extensively as selective catalysts for a variety of different hydrogenation reactions. To study the structure-activity relationships of bimetallic nanomaterials, several bimetallic nanomaterials with tunable sizes and shapes were rationally designed and synthesized in a controlled manner. In a typical example reported by Tsang *et al.* (2008), Pt-Co nanoalloy was prepared for the selective hydrogenation of α,β -unsaturated aldehydes to α,β -unsaturated alcohols.

Pt nanocrystals of specific tailored sizes were decorated with Co atoms in a controlled manner in colloid solution. Using Co-decorated Pt nanocrystals with a critical size range, they successfully achieved the hydrogenation of terminal C=O groups with high activity, whereas the undesirable hydrogenation of the C=C group was totally suppressed as a result of the blockage of the unselective low coordination sites and the optimization of the electronic influences of the Pt nanoparticles of the appropriate size resulting from the Co decoration process.

Coupling reactions

Pd-catalyzed cross-coupling reactions, such as the Heck, Suzuki, and Sonogashira reactions, have become some of the most important organic transformations in synthetic chemistry for forming C–C bonds (Hyotanishi *et al.*, 2011), and the use of Pd nanoparticles in these coupling reactions has been studied extensively (Li *et al.*, 2009; Zhang *et al.*, 2011). Recent studies on these reactions have focused on enhancing the activity, selectivity, and stability of the catalysts used as well as elucidating the catalytic reaction mechanisms by designing a variety of novel Pd-based bimetallic nanomaterials. To facilitate the recovery of the catalyst, reduce the usage of Pd, and improve the overall efficiency of these reactions, we prepared a series of magnetically separable “quasi-homogeneous” Pd-Ni nanoalloys with tunable composition properties using a one-pot wet chemical reaction (Tan *et al.*, 2013). The resulting catalysts not only showed higher catalytic activity than the equivalent amount of Pd nanoparticles for the Suzuki-Miyaura coupling reaction, but also exhibited excellent recyclability.

Hydrodechlorination

In view of environmental hazards associated with chlorinated, toxic organic materials, Ni and several precious metals, including Pd, Pt and Rh, have been widely used either in bulk or in some supported form for the catalytic dechlorination of chlorinated hydrocarbons. Of all of the metals tested for this purpose, Pd is one of the most active and selective (Bertolini and Jugnet, 2002). Various Pd-based bimetallic nanomaterials have recently been used for the treatment of chlorinated hydrocarbons, where they exhibit high dechlorination efficiencies. For example, Pd-Fe bimetallic nanoparticles

prepared by the chemical precipitation method in the liquid phase were found to be efficient for the catalytic dechlorination of chlorinated methanes. Catalytic dechlorination of hexachlorobenzene by Pd-Fe bimetallic particles proceeded at a faster rate than it did with Fe particles. By measuring different chlorinated intermediates and products, it has been possible to propose different pathways for the catalytic dechlorination reactions of hexachlorobenzene by Fe and Pd-Fe particles.

Amidation

In view of the importance of the development of powerful green catalysts and the common presence of amide bonds in natural products and synthetic compounds, Soulé *et al.* (2011) studied amide bond forming reactions between alcohols and amines catalyzed by Au-M (M = Fe, Co, Ni) nanoparticles using molecular oxygen as a terminal oxidant. A wide variety of alcohols and amines, including aqueous ammonia and amino acids, could be used for this amide bond forming reaction using the optimized Au-Co catalyst. The catalyst could also be recovered and reused several times without any loss in activity.

Reductive amination

The direct synthesis of useful molecules from simple starting materials using one-pot reactions is of particular importance in synthetic organic chemistry because of the inherent advantages associated with this approach. In this regard, metal nanoparticles (Pd, Pt) have been used to catalyze the direct one-pot reductive C-N coupling reactions of carbonyl compounds with nitroarenes (Soulé *et al.*, 2011; Hu *et al.*, 2011). The optimum catalyst afforded a wide substrate scope and excellent recyclability as well as high

activity and selectivity under ambient conditions.

Hydrogenolysis

In hydrogenolysis of diols the Ru-Re catalysts showed much higher activity than the Ru catalysts with the Re having an obvious promoting effect on the performance of the catalysts. The coexistence of the Re and Ru components on these supports effectively changed the respective redox behavior of the individual materials on the supports, and therefore indicated the existence of a synergistic effect between the Ru and Re species on the bimetallic catalysts. To evaluate the influence of Re-Re on the reaction during the hydrogenolysis of glycerol, the hydrogenolysis reactions of some other products, including 1,2-propanediol, 1,3-propanediol, 1-propanol, and 2-propanol, were also examined over the Ru and Ru-Re catalysts. The results demonstrated that glycerol preferred to be converted to 1,2-propanediol over the Ru-Re catalyst rather ethylene glycol, whereas 1,2-propanediol and 1,3-propanediol preferred to be converted to 1-propanol over the same catalyst.

Conclusion

Nanomaterials have emerged as green catalysts that offer new opportunities for the development of a sustainable chemical industry. This article provides an overview of some of the latest developments relating to bimetallic nanomaterial catalyzed organic reactions, with particular emphasis on the oxidation of alcohols, hydrogenation of various organic molecules, and C–C bond forming reactions. Despite the great success of bimetallic nanomaterials in terms of their application to oxidation, hydrogenation, and coupling reactions, they have not yet found a

wider application in the reactions for the synthesis of complex molecule. Furthermore, reports pertaining to the use of bimetallic nanomaterials in asymmetric organic synthesis are rather scarce, and significant scope therefore exists for developing a greater understanding of the fundamental properties and practical applications of these materials. During the course of the last decade, the relationships between the catalytic properties (e.g., activity, selectivity, and durability) of bimetallic nanomaterials and their structural characteristics in various reactions have been studied in great detail by many groups, and several key influencing factors have been identified, including surface structure, composition, size, and morphology. It is essential that a thorough understanding of the different types of mechanism available for bimetallic nanocatalysis is developed. One of these mechanisms is the nucleation and growth mechanism for the preparation of bimetallic nanomaterials. Briefly, attention should be focused on understanding the underlying chemistry and identifying effective methods for achieving precise control over the formation process involved in the conversion of individual atoms to the bimetallic nanomaterials. The second of these mechanisms is the catalytic reaction mechanism. Reaction kinetics studies, theoretical modeling, catalyst surface characterization, and the validation of reaction intermediates would be beneficial for this particular mechanism to allow for the design of more effective catalysts, although these studies would ultimately require interdisciplinary collaborations. With the help of computational studies in catalysis, researchers would also be able to screen catalysts on a computer and design more effective catalysts. To replace or even partially replace the traditional industrial noble-metal catalysts (i.e., Pd/C and Pt/C),

researchers are concentrating on developing a variety of promising bimetallic nanomaterials through the rational design of novel nanostructures and the exploration of new catalytic reactions based on thermodynamic and kinetic studies of the different reaction processes. Although the practical application of bimetallic nanomaterials in an industrial context is still some years away, the future development of bimetallic nanocatalysis may significantly benefit from the controllable synthesis of novel bimetallic nanomaterials, as well as a deeper understanding of the mechanisms associated with these reactions and further progress towards computational studies of these catalysts.

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