Review Article

Heterogeneous Metal Catalysts for Oxidation Reactions

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Oxidation reactions may be considered as the heart of chemical synthesis. However, the indiscriminate uses of harsh and corrosive chemicals in this endeavor are threating to the ecosystems, public health, and terrestrial, aquatic, and aerial flora and fauna. Heterogeneous catalysts with various supports are brought to the spotlight because of their excellent capabilities to accelerate the rate of chemical reactions with low cost. They also minimize the use of chemicals in industries and thus are friendly and green to the environment. However, heterogeneous oxidation catalysis are not comprehensively presented in literature. In this short review, we clearly depicted the current state of catalytic oxidation reactions in chemical industries with specific emphasis on heterogeneous catalysts. We outlined here both the synthesis and applications of important oxidation catalysts. We believe it would serve as a reference guide for the selection of oxidation catalysts for both industries and academics.

1. Introduction

Oxidation reactions play a pivotal role in chemical industry for the production of many crucial compounds [1]. For example, selective oxidation of alkyl substituted benzene produces alcohol and ketones which have significant biological and mechanistic interest in modern organic synthesis [2]. Ethylbenzene is a representative compound of various linear and phenyl-substituted alkanes and is a model substrate to study alkane oxidation reactions. The oxidation products of ethylbenzene include acetophenone and 1-phenylethanol which have been used as precursors for the synthesis of a wide variety of drugs, such as hydrogel [3], optically active alcohols [2], hydrazones [4], benzalacetophenones (chalcones) [5], tear gas, and resins [6].

In the past, efforts were made for the oxidation of alkyl substituted benzene to useful products such as benzylic and allylic ketones by adding stoichiometric amounts of strong oxidants such as chromium (IV) reagents, permanganates, *tert*-butyl hydroperoxide (TBHP), selenium oxide (SeO_2), ruthenium (VIII) oxide, hydrogen peroxide, nitric acid, and oxygen [7–9]. However, most of these chemicals are either toxic or corrosive to reactor wall, unstable in atmospheric conditions, nonspecific in actions, which produce many undesirable side products, and that increases the purification cost and environment pollutant [7–9]. These traditional transformation schemes are also time consuming and cannot be recycled [10].

The green chemistry approaches must meet health and environmental safeties and use very little chemicals reducing both cost and time [11]. Catalytic approaches might be considered as green since specific chemical transformation could be achieved within very short time with the addition of very little catalysts, significantly reducing production cost as well as health and environmental risks [12, 13]. According to the North American Catalysis Society, approximately 35% of global GDP rest on catalysts and the use of catalysts in industry are increasing 5% per year [14]. Currently, more than 60% of chemical synthesis and 90% of chemical transformations in chemical industries are using catalysts [15, 16]. In 2013, the sales of catalysts were between 15.5 billion USD and the turnover in industries using catalyst was 14 trillion USD.

Homogeneous catalyst has been extensively used in the oxidative process for the manufacturing of bulk as well as fine chemicals. This is because of its efficiency in bringing huge influences in chemical conversion via the same phase catalysis reaction [17]. In the recent time, some transition metal ion complexes have shown high selectivity, efficiency,

TABLE 1: Major features, advantages, and disadvantages of the commonly used support materials.

Supports materials	Features	Advantages	Disadvantages	References
Alumina	(1) Hardness (2) High melting point and high compression strength (3) Resistant to abrasion and chemical attack (4) High thermal conductivity	(1) Thermally stable (2) Randomly ordered (3) High surface area and pore volume (4) Well-ordered pore (5) Narrow pore size	(1) Difficult to control the hydrolysis rate of aluminum precursors	[73]
Silica	(1) Tendency to form large networks (2) Found in nature and living organisms (3) Hardness	(1) High efficiency (2) High selectivity (3) Highly stable (4) Mechanical strength	(1) Low compatibility (2) Formation of aggregates/agglomerates	[74]
Zeolite	(1) Microporous (2) Inertness (3) Excellent electron conductivity	(1) Highly effective (2) Less or no corrosion (3) No waste or disposal problems (4) High thermo stability (5) Easy set-up of continuous processes (6) Great adaptability to practically all types of catalysis	(1) Irreversible adsorption or steric blockage of heavy secondary products. (2) Impossibility of using microporosity (3) Difficult to exploit the shape selectivity	[75, 76]
Carbon	(1) Nonmetallic (2) Tetravalent (3) Porous structure	(1) High mechanical strength (2) Large surface area (3) Excellent electron conductivity (4) Good elasticity (5) Thermal stability (6) Inertness	(1) High temperature physical activation (2) Expensive (3) Emission of greenhouse gasses during pyrolysis	[77, 78]

and reproducibility to catalyze the reaction under mild conditions. The single catalytic entity in homogeneous catalysts can act as a single active site which can speed up reaction and reduce the reaction time [18]. However, homogeneous catalytic processes produce huge waste materials, significantly disrupting the environmental and ecological stability [19–21]. One of the main disadvantages to the use of these types of catalysts is the ease of separating of the comparatively affluent catalysts from the reaction mixtures at the end of reaction [9, 19, 22]. Homogeneous catalysts also cause corrosion to the industrial materials and some of them are deposited on the reactor wall. To get rid of these problems and minimize environmental hazards, the homogenous catalysts could be prepared by the dispersion of metal on an insoluble solid supports via covalent anchoring to keep the metal on the surface where catalysis reaction takes place [18, 22].

Heterogeneous catalyst is considered to be a better choice for the synthesis of commodity materials [23–25]. Nowadays, silica, carbon, clay, zeolite, metal oxide polymers, and other mesoporous materials are being used as inorganic solid supports [26, 27]. Supported materials can be obtained as complexes with transition metals and Schiff base ligands by heterogenization process [28]. The application of supported polymers in catalytic oxidation has gained much attention because of their inertness and nontoxic, nonvolatile, and recyclable criteria [29]. Among inorganic supports,

the mesoporous materials have been proven to be ideal catalyst supports due to their three-dimensional open pore network structures, high surface area and porosity, high reusability and heat stability, and uniform and interconnected pores which offer a reliable and well-separated atmosphere for the deposition of dynamic components and interactive surfaces between the catalysts and reactants [30–38]. Various support materials along with their major features are presented in Table 1.

Heterogeneous catalysts promote oxidation reactions via attracting oxygen from oxidants, such as TBHP (*tert*-BuO$_2$H) and HP (H$_2$O$_2$) [39, 40]. In the last decade, TBHP has been used as oxidant for various oxidation reactions such as alkyl benzene and benzyl alcohol oxidation. In this review, we described heterogeneous catalysts, their synthesis schemes on various supports, and applications in selected oxidation reactions. The comparative features of homogeneous and heterogeneous catalysts are presented in Figure 1.

2. Heterogeneous Catalysts

In heterogeneous catalysis reaction, the catalysts and reactants exist in different phases. In reality, the vast majority of heterogeneous catalysts are solids and the vast majority of reactants are either gases or liquids [14]. A phase separation catalysis reaction greatly helps in reactant, product, and
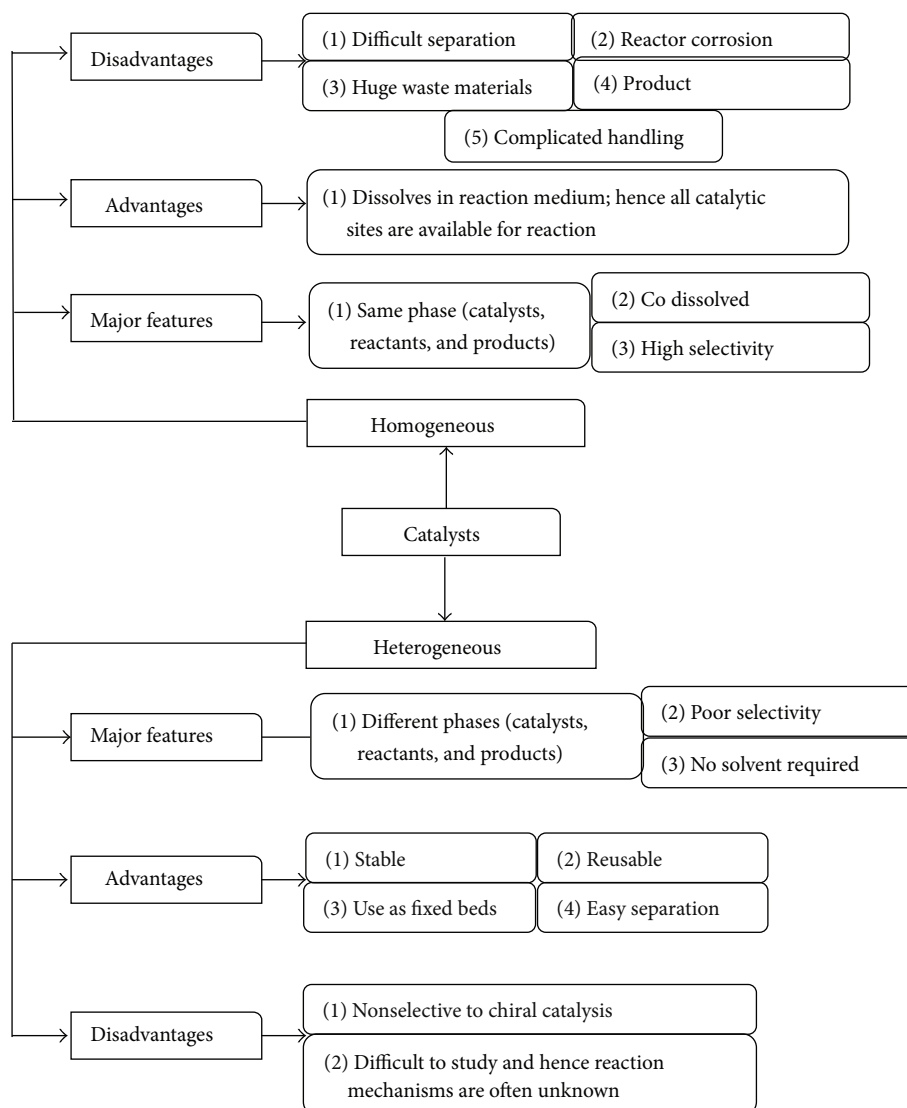
FIGURE 1: Special features, advantages, and disadvantages of homo- and heterogeneous catalysts.

catalyst separation at the end of the reaction. Heterogeneous catalysts are also easier to prepare and handle. These catalysts consist of fine nanosized powders supported on technically inert oxide substrates exhibiting all possible crystallographic faces. The catalyst is often a metal to which chemical and structural promoters or poisons are added to enhance the efficiency and/or the selectivity. Currently, heterogeneous catalysis is dominating in industries for chemical transformation and energy generation. Approximately 90% of all industrial practices indulge in heterogeneous catalysis. The most recent applications of heterogeneous catalysts are summarized in Table 2.

3. Heterogeneous Metal Catalysts in Oxidation Reactions

Over the last few decades, scientists have paid tremendous attention to heterogeneous catalysts to overcome the limitations of their homogeneous counterparts to increase products yields and minimize side reactions. Herein, we reported a summary of selected oxidation reactions catalyzed by supported metal catalysts.

3.1. Conversion of Glucose to Gluconic Acid. Recently, the aerobic oxidation of glucose to gluconic acid (Figure 2) has gained much consideration because of its water-soluble cleansing properties and application in food additives and beverage bottle detergents [41]. In the past, the oxidation of glucose was carried out via biochemical pathways which are cumbersome, multistep process, not recyclable, and expensive [42]. The development of catalytic route is probably an alternative pathway for the large scale production of gluconic acid from glucose. In 1970s, researchers used to dope Pt or Pd onto some heavy metals such as bismuth. However, several limitations, such as instability, poor selectivity, and low conversion rate, were encountered with this procedure

TABLE 2: Recent scenario in heterogeneous catalysis.

Year	Catalyst	Method of preparation	Major applications	References
2013	Fe nanocatalyst	Immobilization	Ethylbenzene, cyclohexene, and benzyl alcohol oxidation	[18]
2013	Au/Al$_2$O$_3$, Au/C	Deposition-precipitation, cationic adsorption	Glucose oxidation	[79]
2013	Au/Pt bimetallic nanoparticles	—	Glucose oxidation	[80]
2013	Gold nanoparticles supported on Mg(OH)$_2$ nano sheets	Colloidal deposition	CO oxidation	[81]
2013	Au/TiO$_2$ supported on ferritic stainless steel monoliths	Direct anionic exchange	CO oxidation	[82]
2013	Nanoporous gold	Electrolytic dissolution	CO oxidation	[83]
2013	P123-stabilized Au-Ag alloy	Co reduction	Benzyl alcohol oxidation	[84]
2013	Alumina-supported gold-ruthenium bimetallic catalysts	Incipient wetness Impregnation Deposition Precipitation	CO oxidation	[54]
2013	Au/CuO catalysts	Coprecipitation	Alcohol oxidation	[85]
2013	Cerium modified silver	Impregnation	Alkyl aromatic compounds	[86]
2013	Pd-Au catalyst	Dealloying	Methanol electrooxidation	[87]
2013	Au/ZnO and Au/TiO$_2$ catalysts	Colloidal deposition	Methanol oxidation	[88]
2013	Microstructured Au/Ni-fiber catalyst	Incipient impregnating	Alcohol oxidation	[89]
2013	Nanocrystalline Ag and Au-Ag alloys supported on titania	Deposition Precipitation	CO oxidation	[90]
2013	Nanosized Au supported on 3-D ordered mesoporous MnO$_2$	Deposition Precipitation	Oxidation of carbon monoxide, benzene, and toluene	[91]
2013	Au/FeO$_x$	Coprecipitation	CO oxidation	[92]
2013	Nanosized ruthenium particles decorated carbon nanofibers	Sol gel	p-Cymene oxidation	[93]
2012	Au/C	Incipient wetness impregnation	Glucose oxidation	[94]
2012	CeAlPO-5 molecular sieves	—	Diphenylmethane oxidation	[10]
2012	Nanosized gold on SiO$_2$	Stöber	Cyclohexene and D-glucose oxidation	[95]
2012	Au/SiO$_2$	Dispersion	Silanes oxidation	[47]
2012	Nano gold-mesoporous silica	—	CO oxidation, benzyl alcohol oxidation	[96]
2012	Nanosized gold	Dispersion	Alkyl benzene oxidation	[40]
2012	Ag/SBA-15	Impregnation	Alkyl substituted aromatics	[35]
2012	Bimetallic Au-Pd/MgO	Sol-immobilization (SI) and adsorption-reduction (AR)	Benzyl alcohol oxidation	[97]

TABLE 2: Continued.

Year	Catalyst	Method of preparation	Major applications	References
2012	Inverse Fe$_2$O$_3$/Au(111) model catalysts	—	CO oxidation	[98]
2012	Silica-supported Au-Cu alloy	—	Alcohol oxidation	[99]
2012	Gold nanoparticles supported on MgO	Deposition-precipitation	Alcohol oxidation	[100]
2012	Silica-supported Au-CuO$_x$	Oxidative dealloying	Ethanol oxidation	[101]
2011	Au/Al$_2$O$_3$	Incipient wetness impregnation	Glucose oxidation	[102]
2011	Au-Pd/C	Impregnation	Glyoxal and glucose oxidation	[103]
2011	Pd-Te supported catalysts	Repeated impregnation	Glucose oxidation	[104]
2011	Gold nanoparticles supported on functionalized mesoporous silica	One-pot Synthesis	Cyclohexane oxidation	[105]
2011	Silica supported cobalt (II) salen complex	Immobilization	Alkyl benzene oxidation	[70]
2011	Gold nanowires	—	Oxidation of benzylic compounds	[106]
2011	Cu$_{3/2}$[PMo$_{12}$O$_{40}$]/SiO$_2$	Incipient wetness impregnation	Benzylic alcohol	[107]
2010	Gold nanoparticles deposited on cellulose	Deposition-reduction, grinding method	Glucose oxidation	[41]
2010	Metalloporphyrin bound to silica	Immobilization	Ethylbenzene oxidation	[68]
2010	Hydrophobized palladium	Vapor deposition	Glucose oxidation	[108]
2010	Supported gold catalysts	Colloidal gold deposition	CO oxidation	[109]
2010	Au/HMS catalysts	Impregnation and direct synthesis	Benzyl alcohol oxidation	[63]
2010	Mobilized gold nanoparticles	Gold sol	Secondary alcohols oxidation	[67]
2010	Mesoporous Co$_3$O$_4$ and Au/Co$_3$O$_4$ catalysts	Nanocasting	Ethylene oxidation	[110]
2010	Metal-organic framework supported gold nanoparticles	Colloidal deposition	Alcohol oxidation	[111]
2010	Pt/Al$_2$O$_3$	Impregnation	Heavy hydrocarbons oxidation	[112]
2009	Au/TiO$_2$	Deposition-precipitation	Alcohol oxidation	[113]
2009	Co(AcO)$_2$/Mn(AcO)$_2$	Direct condensation	p-xylene oxidation	[114]

TABLE 2: Continued.

| Year	Catalyst	Method of preparation	Major applications	References
2009	Nickel substituted copper chromite spinels	Coprecipitation	Alkyl substituted benzene oxidation	[9]
2007	Gold catalysts	Deposition-precipitation	Alcohol oxidation	[115]
2007	MCM-48 molecular sieve modified with SnCl$_2$	Post-synthesis modification	Alcohol oxidation	[65]
2007	CuO-impregnated mesoporous silica	Impregnation	Benzene oxidation	[116]
2006	Supported gold catalysts	Deposition-precipitation	Alcohol oxidation,	[117]
2006	Au-CuO/Al$_2$O$_3$, Pt/Al$_2$O$_3$ catalysts	Deposition-precipitation, impregnation	Propene and propane oxidation	[118]
2006	Manganese containing mesoporous MCM-41 and Al-MCM-41 molecular sieves	Impregnation	p-isopropyltoluene oxidation	[119]
2005	Gold catalysts	—	Alcohol oxidation	[120]
2005	Au/C	Immobilization	Glucose oxidation, Alcohol oxidation	[64]
2005	Gold immobilized mesoporous silica	Immobilization	Cyclohexane oxidation	[121]
2005	Nitrous oxide over MFI zeolites	Hydrothermal	Benzene oxidation	[122]
2005	CoAPO-5 molecular sieves	Hydrothermal	Cyclohexane oxidation	[123]
2004	Carbon-supported gold	Gold sol	Glucose oxidation	[124]
2004	Mn-containing MCM-41	Impregnation	Ethylbenzene oxidation	[72]
2003	CoO$_x$/CeO$_2$	Coprecipitaion	Carbon monoxide oxidation	[125]
2002	Gold catalysts	Immobilization	Glucose oxidation	[126]
2002	Mn (Salen)/MCM-41	—	Olefins epoxidation	[127]
2002	Nanostructured CuO$_x$/CeO$_2$	Gas-condensation	Carbon monoxide oxidation	[128]
2002	Nano-Au Catalysts	—	Carbon monoxide oxidation	[55]
2001	Au/TiO$_2$, Au/TiO$_2$/SiO$_2$	Deposition-precipitation	Propene epoxidation	[129]
2000	Gold-titania catalysts	Deposition-precipitation	Propylene oxidation	[130]
1999	Gold dispersed on TS1 and other titanium-containing supports	Dispersion	Propene epoxidation	[131]
1998	Gold-titania catalysts	Deposition-precipitation	Propylene epoxidation	[61]
1996	Heteropoly catalysts containing Ru(III) and Rh(III) particles	—	Alkane oxidation	[132]
1996	Gold supported on ZnO and TiO$_2$	Coprecipitation & Deposition-precipitation	Carbon monoxide oxidation	[133]
1996	Au-TiO$_2$	Incipient wetness impregnation	Carbon monoxide oxidation	[134]
1995	Bismuth promoted palladium catalysts	Ion exchange	Glucose oxidation	[42]
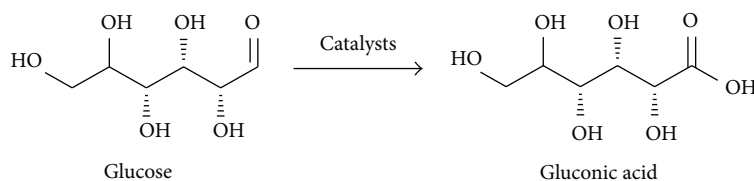
FIGURE 2: Conversion of glucose to gluconic acid.
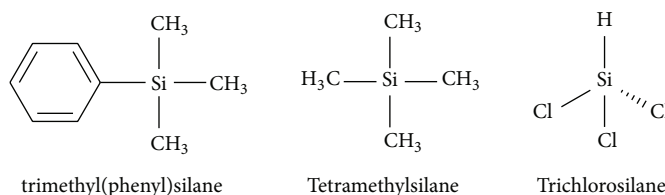
SCHEME 1
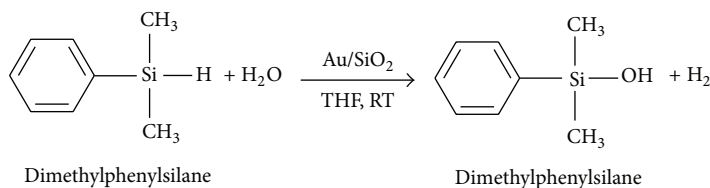
SCHEME 2

without any supporting materials [42]. On the other hand, bismuth on palladium or Pt/Pd on carbon supports demonstrated high selectivity and stability and excellent conversion rate, overcoming the limitations of the heavy metal supports. Some features such as catalyst type and the role of bismuth support are still a disputed issue [42].

Prati and Rossi (1997) [43] studied the oxidation of 1,2-diols and found excellent selectivity with gold catalyst over platinum and palladium catalysts. The gold catalyst showed unusual selectivity in the oxidation of alcohol to its corresponding carboxylates whereas Pd or Pt showed lower selectivity to oxidize ethane-1,2-diol. From this observation, they also concluded that Au is less sensitive to overoxidation and/or self-poisoning than Pd or Pt. Gold clusters and nanoparticles (NPs) deposited on the metal oxide surface such as Al_2O_3 and ZrO_2 demonstrated unexpected catalytic activity in the oxidation of glucose with better turnover frequency (TOF, reaction rate per Au atom surface). In addition to carbon and metal oxide supports, some inorganic polymers such as silica could be used as catalytic supports for small Au nanoparticles (>10 nm in diameter) [43]. The catalytic effect of Au nanoparticles (2.5 nm) held by polymer gel was demonstrated by Ishida et al., [44]. Polymer supported AuNPs exhibited higher catalytic performance than Au/C in the oxidation of primary alcohols such as benzyl alcohol to benzaldehyde in absence of base [45]. The catalytic activity of various catalysts for glucose oxidation is summarized in Table 3.

3.2. Selective Oxidation of Silanes to Silanols. Silane is an inorganic compound having the silicon atom with chemical formula SiH_4. It is a colorless flammable gas with a sharp and repulsive smell, somewhat similar to that of acetic acid. Silane has interest as a precursor of silicon metal. Silane may also be referred to many compounds containing silicon, such as trichlorosilane ($SiHCl_3$), trimethyl(phenyl)silane ($PhSi(CH_3)_3$), and tetramethylsilane ($Si(CH_3)_4$) (Scheme 1).

The oxidation of silane to corresponding silanols (as for example dimethylphenylsilane to dimethylphenylsilanol, Scheme 2) is a key reaction to manufacture building blocks for the synthesis of silica based polymers [46] and nucleophilic couplers in organic synthesis. In the past, silanols synthesis was often carried out by stoichiometric oxidation of organosilanes, hydrolysis of halosilanes, or alkali treatment of siloxanes which incurred environmental hazards. In contrast, the catalytic oxidation of silanes with water is an ecofriendly process since it produces silanols with high selectivity, producing only hydrogen as a by-product. Supported gold nanoparticles have shown higher catalytic activity and selectivity on silane oxidation over other transition metal catalysts [47]. Mitsudome et al. [48] oxidized aliphatic silanes to silanols using hydroxyapatite supported AuNPs in water at 80°C. Nanoporous gold also showed high reactivity and selectivity towards silanes in acetone at room temperature [49].
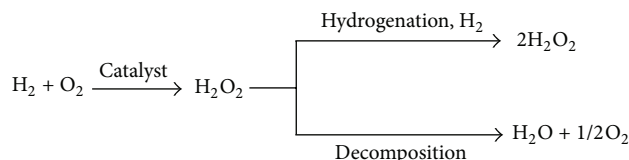
Recently, John et al. [50] have synthesized carbon nanotube-supported gold nanoparticles which showed turnover frequency (TOF) of 18,000 h^{-1} for silane oxidation in tetrahydrofuran (THF) at room temperature. However, the preparation of Au CNT (carbon nanotube) hybrids involved a multistep layer-by-layer assembly which needed expensive reagents which have limited its practicability. Li et al. [47]

TABLE 3: Oxidation of glucose by various catalysts.

Name of catalysts	Preparation method	Substrate	Oxidant	Reaction condition Reaction time (h)	Reaction temperature (°C)	pH	Solvent	Main product	Selectivity (%)	References
Gold nanoparticles on cellulose	Deposition-reduction	Glucose	O_2	—	60	9.5	Water	Gluconic acid	—	[41]
Au/Al$_2$O$_3$	Deposition-precipitation		O_2	7	60	9.0	Water	Gluconic acid	97	[79]
Au/C	Cationic adsorption		O_2	7	60	9.0	Water	Gluconic acid	97	[79]
Au-Pd/C	Impregnation		O_2	20	50	9.25	—	Gluconic acid	—	[103]
Au/Al$_2$O$_3$	Incipient wetness impregnation		H_2O_2		40	9.0	—	Sodium D-gluconate	99	[102]
Au/C	Gold sol		—	30	50	9.5	—	Gluconic acid	45	[124]
Nanosized Au/SiO$_2$	Stöber		H_2O_2	24	30	9.2	Water	Gluconic acid	80	[95]
Pb-Te/SiO$_2$	Repeated impregnation		O_2	1.5	60	9.0	—	Gluconic acid	88.4	[104]
Au/Pt bimetallic nanoparticle	Vacuum drying		O_2	2	60	9.5	—	Gluconic acid	—	[80]

TABLE 4: Comparison of supported gold catalysts for the oxidation of triethylsilane [47].

| Catalysts | Substrate | Solvent | Reaction condition | | | Conversion rate (%) | Yield (%) |
			Reaction temperature	Time (min)	Au/substrate (mol%)		
Au/SiO_2		Water	25°C	3	0.4	99	99
Au/TiO_2		Water	25°C	3	0.4	81	81
Au/Fe_2O_3	Triethylsilane	Water	25°C	3	0.4	36	36
Au/ZnO		Water	25°C	3	0.4	89	89
Au/CeO_2		Water	25°C	3	0.4	98	98

$$H_2 + O_2 \xrightarrow{\text{Catalyst}} H_2O_2 \begin{array}{c} \xrightarrow{\text{Hydrogenation, } H_2} 2H_2O_2 \\ \\ \xrightarrow{\text{Decomposition}} H_2O + 1/2 O_2 \end{array}$$

SCHEME 3: Hydrogen peroxide formation, hydrogenation, and decomposition.

prepared silica supported gold catalysts for the selective oxidation of silanes. However, they observed that silica supported gold catalysts are more active than reducible oxides (TiO_2, Fe_2O_3, CeO_2, etc.) supported AuNPs. Highly dispersed silica supported gold catalysts override the reducible oxides supported AuNPs due to superior adsorption of silane substrate on silica support. Surprisingly, for the oxidation of dimethylphenylsilane in THF at room temperature, the Au/SiO_2 catalyst afforded a TOF of 59,400 h^{-1}, which is the highest TOF reported to date.

The other oxide supported gold catalysts, such as Au/TiO_2, Au/ZnO, and Au/Fe_2O_3, were less active than Au/SiO_2, and they afforded a maximum conversion of 90%. However, the activity of Au/CeO_2 catalyst was very similar to the Au/SiO_2 catalyst (Table 4).

3.3. Oxidation of Hydrogen to Hydrogen Peroxide (H_2O_2). H_2O_2 is an essential chemical which has long been used mainly as strong oxidant in various oxidative reactions and bleaching agent as well as a disinfectant. It is a green oxidant since its sole by-product is water. In the current decades, a lot of attention has been paid to the green catalysts and green chemicals to ensure safety issues in health and environment. Industries have been using supported Pd catalysts for more than 90 years for the direct synthesis of H_2O_2 from H_2 and O_2. However, the synthesized H_2O_2 is unstable and undergoes low-temperature decomposition or hydrogenation to water (Scheme 3) [51]. Recently, Edwards et al. [52] used Au-catalysts synthesized via coprecipitation or deposition-precipitation method and found very low H_2O_2 conversion rate. They also observed that the addition of Au to Pd catalysts by impregnation enhances H_2O_2 formation. They compared five different catalyst supports, namely, Al_2O_3, Fe_2O_3, TiO_2, SiO_2, and carbon, and found the high conversion with carbon-supported Au-Pd (Au-Pd/C).

In 2010, Song et al. [53] observed that $KMnO_4$ treated activated carbon in an acidic solution enhances H_2O_2 production (78%) from hydroxylamine due to the creation of surface active quinoid species during oxidation. Structure and surface analyses revealed that $KMnO_4$ treatment produced more phenolic but less carboxylic groups on the activated carbon under acidic condition, confirming the crucial role of the quinoid groups. It was also proposed that the quinoid groups served as electron acceptors and redox mediators in the formation of H_2O_2 [53].

3.4. Carbon Monoxide (CO) Oxidation. In the last decade, CO oxidation has become an important research area because of its involvement in a number of processes, such as methanol synthesis, water gas shift reaction, carbon dioxide lasers, and automotive exhaust controls [54]. Carbon monoxide is a lethal gas for animal life and toxic to the environment [55]. The oxidation of CO is a difficult process and hence a highly active oxidation catalyst is required for its efficient removal from the environment [55]. In the past, the gold was considered to be inert for CO oxidation [56].

However, Haruta et al. [57] demonstrated that highly dispersed gold prepared on various metal oxide supports by coprecipitation and deposition-precipitation methods is highly active in CO oxidation even below 0°C temperature. They found that catalytic performance significantly depends on the catalysts preparation methods and the highest activity was demonstrated by TiO_2 supported gold or platinum catalysts prepared by deposition-precipitation (DP). The gold catalysts prepared by photodeposition (PD) and impregnation (IMP) methods were less active than those prepared by deposition-precipitation. This is because the catalysts prepared by DP method contain higher loading of Au (>2 wt%) on smaller particles and are with better dispersion. Collectively, these features enable the catalyst to show higher activity, oxidizing ~100% of CO at temperatures below −20°C. In 1997, Yuan et al. [58] synthesized highly active gold catalysts for CO oxidation simply by grafting Au-phosphine complexes (AuL_3NO_3 or Au_9L_8 $(NO_3)_3$; L = PPh_3) onto precipitated $Ti(OH)_4$ surfaces. This Au-phosphine-$Ti(OH)_4$ complex was active even below the 0°C. Apart from this, Na^+ ions positively and Cl^- ions negatively affect the Au-catalyzed
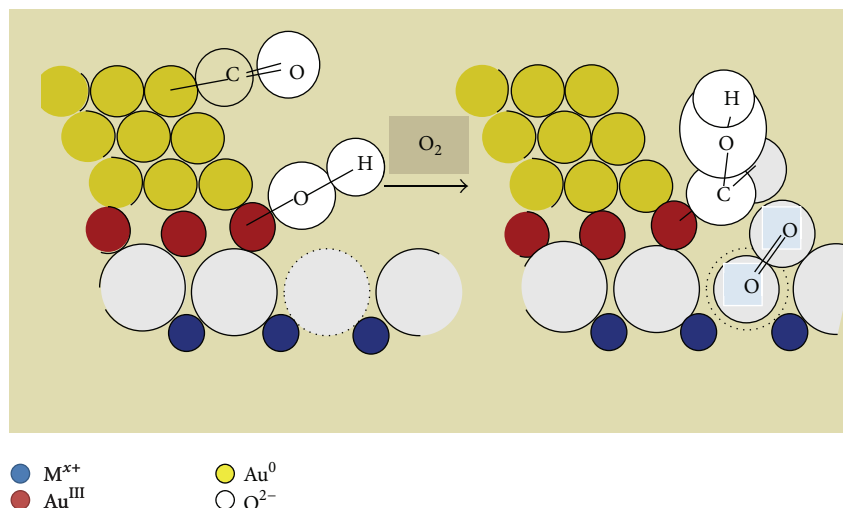
FIGURE 3: Plausible mechanism for CO oxidation on oxide supported gold catalyst. On the left, a CO molecule is chemisorbed onto a low coordination number gold atom (yellow sphere), and a hydroxyl ion is moved from the oxide support (pink sphere) to an Au (III) ion, creating an anion vacancy. On the right they have reacted to form a carboxylate group, and an oxygen molecule occupies the anion vacancy as O^{2-} (white sphere). This then oxidizes the carboxylate group by abstracting a hydrogen atom, forming carbon dioxide, and the resulting hydroperoxide ion HO_2^- then further oxidizes carboxylate species to form another carbon dioxide, restoring two hydroxyl ions to the support surface, completing the catalytic cycle. (Adapted with permission from Springer) [145].

$$CH_3CH=CH_2 + O_2 + H_2 \xrightarrow{\text{Catalysts}} CH_3CH_2-CH_2 + H_2O$$
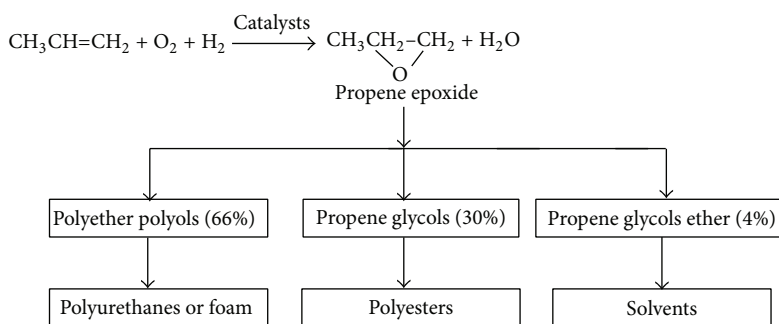
SCHEME 4: Synthetic products from propene epoxidation reaction.

CO oxidation. Figure 3 represents the initial stages of CO oxidation at the edge of an active gold particle.

3.5. Epoxidation of Propene.

The oxidation of propene to epoxide is an important reaction for the synthesis of various industrial chemicals such as polyether polyols (precursor of polyurethane or foams), propene glycol, and propene glycol ethers (Scheme 4) [59]. In the past, chlorohydrin and hydroperoxide mediated processes were used for the synthesis of propene epoxide. Chlorohydrin process produces environmentally hazardous chlorinated by-products and the hydroperoxide process is much expensive and produces styrene and *tert*-butyl alcohol as by-products. Silver catalysts were used in this reaction but poor selectivity and turnover were observed [60]. However, titania supported gold efficiently catalyzed the epoxidation reaction at 30–120°C with more than 90% selectivity in the presence of hydrogen [61].

3.6. Oxidation of Alcohol.

The oxidation of alcohols to its corresponding aldehydes or ketones is a crucial reaction in organic synthesis. Ketones, specially, acetone, are widely used in the production of various organic as well as fine chemicals [62]. Traditional chemical routes use stoichiometric chemicals such as chromium (VI) reagents, dimethyl sulfoxide, permanganates, periodates, or *N*-chlorosuccinimide which are expensive and hazardous. Several homogeneous catalysts such as Pd, Cu, and Ru are found to selectively catalyze alcohol oxidation. However, homogeneous catalysis requires high pressure oxygen and/or organic solvent, incurring cost and environmental burdens [63]. The present ecological deterioration has forced researchers to look for novel and environmentally friendly catalytic schemes for the oxidation of alcohol. Prati and Porta [64] demonstrated that Au/C catalyst shows higher selectivity toward aldehyde in the oxidation of primary alcohols. Subsequently, Endud and Wong [65] synthesized porous Si/Sn bimetallic catalyst through
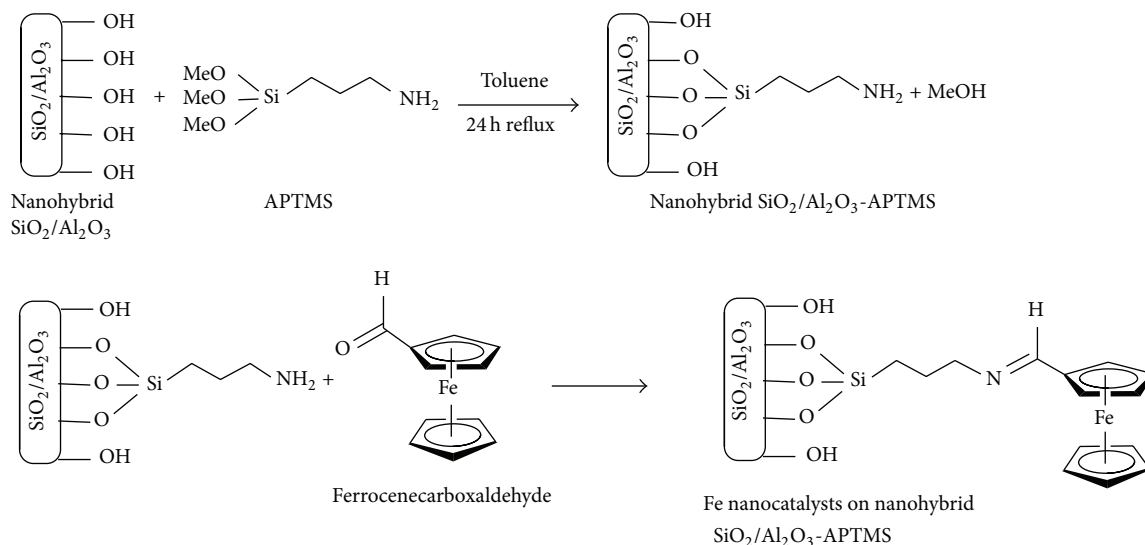
FIGURE 4: Synthesis of heterogeneous Fe nanocatalysts by the immobilization of Fe on functionalized SiO_2-Al_2O_3 mixed oxide 3-aminopropyltrimethoxysilane (3-APTMS). Adapted with permission from Elsevier [18].

postsynthesis modification of rice husk ash as Si precursor and $SnCl_2$ as tin source. Using TBHP oxidant, the tin modified MCM-48 showed much selectivity toward aldehyde or ketone in the oxidation of benzyl alcohols [65].

Chaki et al. [66] looked into the catalytic activity of gold by adding silver (5–30% Ag content) into gold particles for aerobic oxidation of alcohols. It showed that <10% Ag accelerates the catalytic activity of Au. Recently, Kidwai and Bhardwaj [67] described that gold nanoparticles (AuNP) are highly active in alcohol oxidation with hydrogen peroxide as oxidant. They observed that AuNPs, with extended surface area, exhibit higher catalytic activity over others. Additionally, gold catalyzed reactions are free from chemical hazards and toxic solvents and produce water as the only side product. This methodology was a great contribution towards the development of sustainable green chemistry.

4. Heterogeneous Catalysts in the Oxidation of Alkyl Substituted Benzene

In this Section, we described various catalysts, their synthetic schemes, and performance for the oxidation of alkyl substituted benzenes which are an important compound in organic synthesis.

4.1. Fe Nanocatalysts. Habibi et al. [18] synthesized Fe nanocatalyst which oxidized alkyl substituted benzene. They prepared the heterogeneous nano-Fe catalyst on the SiO_2/Al_2O_3 supports through the covalent immobilization of ferrocenecarboxaldehyde which acts as iron source (Figure 4). In the presence of *tert*-butyl hydroperoxide (TBHP) oxidant, this catalyst produces acetophenone, benzaldehyde, and benzoic acid from ethylbenzene with 89% selectivity to acetophenone (Scheme 5).

This catalytic scheme provided certain benefits including the low cost raw materials, commercially available simple
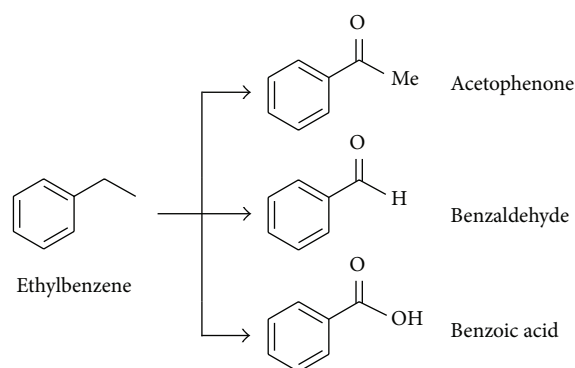
SCHEME 5: Products from the catalytic oxidation of ethyl aromatic with novel Fe nanocatalysts.

chemicals, and catalysts reusability for the further oxidation of ethylbenzene. The side chain carbonyl group is produced by TBHP oxidant without any solvent at a substrate/TBHP ratio of 1 : 1, at 50–120°C in a day.

This novel Fe nanocatalyst exhibited higher conversion rate (>84%) of ethylbenzene with 90% selectivity toward acetophenone which is the precursor of many products such as resins, chalcones, drugs, fine chemicals, and optically active alcohols. The comparative performances of various catalysts for alkyl benzene oxidation are given in Table 5.

4.2. Manganese (III) Porphyrin Complexes in the Oxidation of Alkyl Substituted Benzene. Silica bound manganese (III) porphyrin complexes, [Mn(TMCPP)](TMCPP: 5, 10, 15, 20-*tetrakis*-(4-methoxycarbonylphenyl)-21,23*H*-porphyrin], selectively catalyzes the oxidation of alkyl substituted benzene to its corresponding ketone. Ghiaci et al. [68] synthesized manganese porphyrin complexes by immobilization onto

TABLE 5: Catalysts for alkyl benzene oxidation.

Name of catalysts	Substrate	Oxidant	Reaction time (h)	Reaction temperature (°C)/solvent	Preparation method	Main product	Selectivity (%)	References
Fe nanocatalysts on the surface SiO_2/Al_2O_3		TBHP	24	50/—	Immobilization	Acetophenone	89	[18]
Ag/SBA-15		TBHP	5	90/—	Impregnation	Acetophenone	99	[35]
Nickel substituted Cu chromite spinel		TBHP	8	70/CH_3CN	Coprecipitation	Acetophenone	69	[9]
Silica supported cobalt, NHPI		O_2	24	100/CH_3COOH	Immobilization	Acetophenone	91	[70]
Au/SBA-15	Ethylbenzene	TBHP	36	70/CH_3CN	In situ impregnation	Acetophenone	93	[40]
Mn-containing MCM-41U		O_2	—	350/	Impregnation	Acetophenone	93.6	[72]
[Fe(tpa)(MeCN)$_2$](ClO$_4$)$_2$		O_2	24	75°C/2-butanone	—	Acetophenone	54	[135]
[a]TPFPPFeCl		O_2	24	100/—	—	Acetophenone	82.8	[18]
Fe/MgO, [b]NHPI		O_2	20	25/—	—	Acetophenone	52	[18]
Fe (salen)-[c]POM		H_2O_2	5	80/CH_3CN	—	Acetophenone	100	[18]

[a]Fe (5, 10, 15, 20-tetrakis (pentafluorophenyl)) porphyrin; [b]N-hydroxyphthalimide; [c]Kegging type polyoxometalate (K8SiW11O39) [17]. U = unwashed.
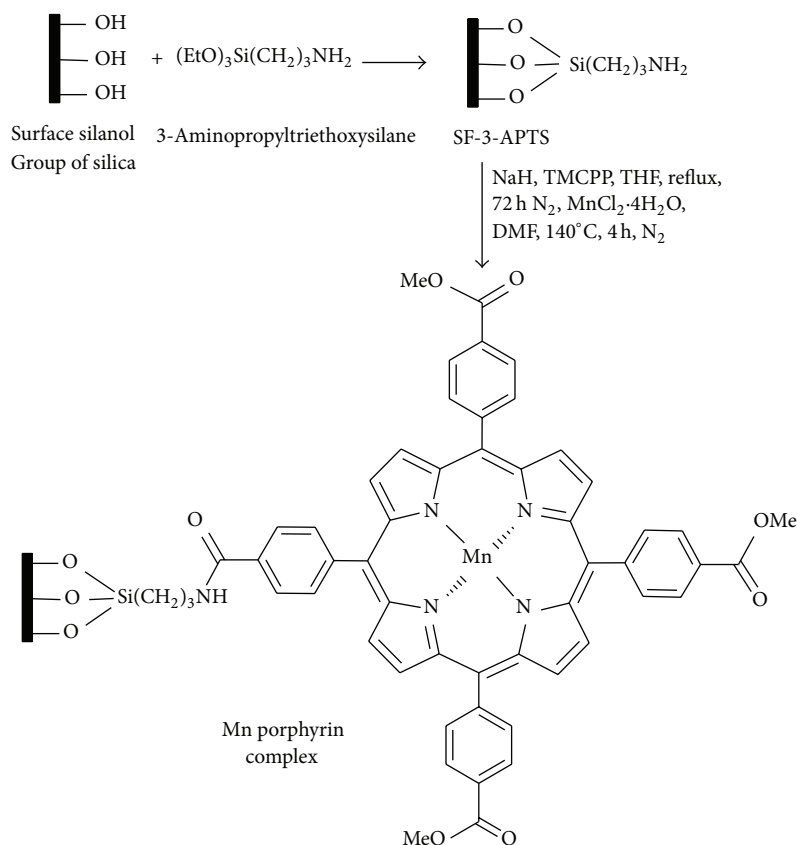
FIGURE 5: The synthetic scheme of manganese porphyrin complex by immobilization on silica support (Adapted with permission from Elsevier [68]).

silica support. This catalyst complex showed high selectivity and efficiency toward hydrocarbon oxidation due to its shape selectivity toward substrate and matrix support that provided special atmosphere for C–H oxidation [69]. For catalysts synthesis, the silica gel was made active at high temperature (500°C) followed by modification with 3-aminopropyltriethoxysilane that acts as silica source under inert gas (N_2) atmosphere. The details of the preparation of this catalyst are described elsewhere (Figure 5). The effects of various parameters such as oxidants, solvents, and temperature on the oxidation of substituted benzene were studied and the maximum catalysis was obtained with TBHP oxidant at 150°C under solvent free conditions.

4.3. Ag/SBA-15 Catalysts in the Oxidation of Alkyl Substituted Benzene. The C–H bond of alkyl substituted benzene can be selectively oxidized to its corresponding ketones by Ag/SBA-15 catalysts with TBHP as oxidant. Recently, Anand et al. [35] synthesized the silica supported Ag catalysts by impregnation method and found that Ag/SBA-15 is an environmentally friendly catalyst for the breaking of alkyl benzene C–H bond. They used tetraethyl orthosilicate as silica source and silver nitrate as silver source. The schematic of the synthetic scheme is given in Figure 6, and the details could be obtained from bibliography [35]. The prepared catalyst showed the best conversion rate in presence of *tert*-butyl hydroperoxide

TABLE 6: Effect of various solvents on the Ag/SBA-15 catalyzed oxidation of alkyl substituted benzene at 90°C in presence of 70% TBHP oxidant [35].

| Solvent | Conversion (%) | Selectivity (%) | |
		Acetophenone	1-phenylethanol
Toluene	92	92	8
DMF	15	80	20
Acetonitrile	85	86	12
Water	65	89	10
No solvent	92	99	1

oxidant with 92% and 99% selectivity towards ketone under solvent free condition (Table 6).

4.4. Nickel Substituted Copper Chromite Spinels. Another form of catalysts, called nickel substituted copper chromite ($Cu_2Cr_2O_5$) spinels, can efficiently catalyze the oxidation of alkyl substituted benzene. George and Sugunan (2008) [9] synthesized nickel substituted copper chromite spinels using copper nitrate, nickel nitrate, and chromium nitrate via coprecipitation method. In the first step, a solution of copper, nickel, and chromium nitrate was prepared in water. The pH of the solution adjusted to 6.5–8.0 with the stepwise addition of 15% ammonium solution under constant stirring.
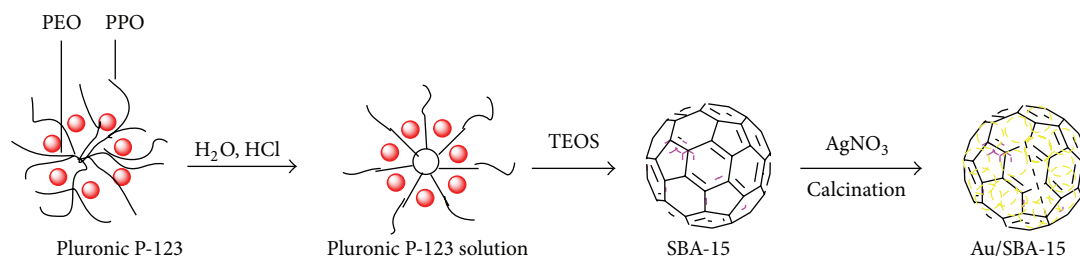
FIGURE 6: Synthesis of Ag/SBA-15 catalysts by impregnation method.
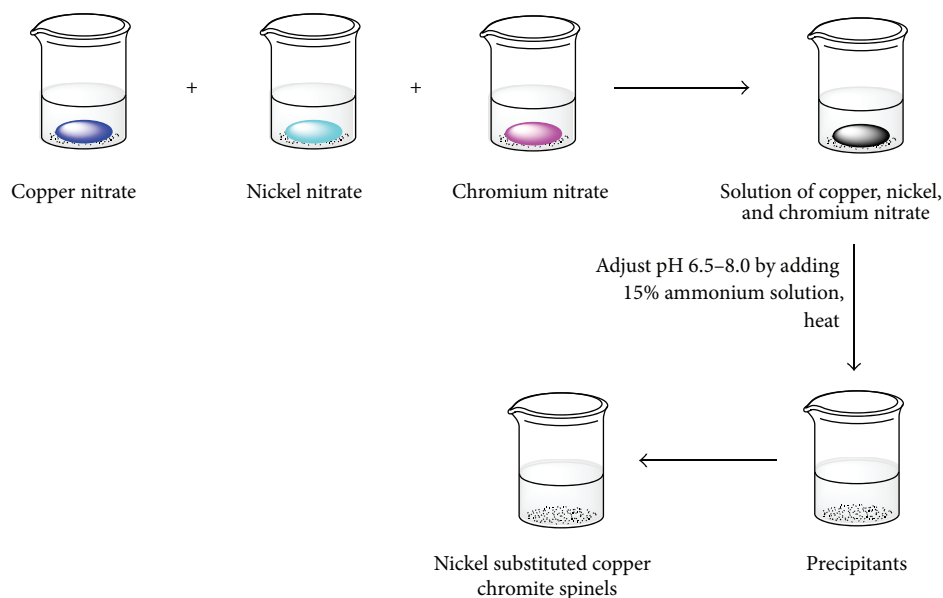

FIGURE 7: Synthesis of nickel substituted copper chromite spinels.

TABLE 7: Recipe for the preparation of various nickels substituted copper chromite spinels [9].

Catalysts composition ($Cu_{1-x}Ni_xCr_2O_4$)	Designation
$CuCr_2O_4$ ($x = 0$)	CCr
$Cu0.75Ni0.25Cr_2O_4$ ($x = 0.25$)	CNCr-1
$Cu0.5Ni0.5Cr_2O_4$ ($x = 0.5$)	CNCr-2
$Cu0.25Ni0.75Cr_2O_4$ ($x = 0.75$)	CNCr-3
$NiCr_2O_4$ ($x = 1$)	NCr

The precipitate was maintained at 70–80°C for 2 h and aged for 24 h. Finally, the precipitate was filtered, washed, and dried at 353 K for 24 h and calcined at 923 K for 8 h to get the spinels. Figure 7 depicts the complete procedure for the synthesis of nickel substituted copper chromite spinel. The recipe of George and Sugunan (2008) [9] for the preparation of nickel substituted copper chromite spinels catalyst is given in Table 7.

Catalytic activity of each spinel for the oxidation of ethylbenzene was studied in detail [9] and it was found that CNCr-2 type chromite spinel provides the maximum conversion rate (56.1%) with 68.7% selectivity towards acetophenone (Table 8) under solvent free conditions [9]. Nickel substituted

chromites were compared with those simple chromites, and the nickel chromites demonstrated superior activity.

4.5. Silica Supported Cobalt (II) Salen Complex. The aerobic oxidation of alkyl substituted benzene was successfully carried out over silica supported cobalt (II) salen complex in presence of O_2 in *N*-hydroxyphthalimide (NHPI) solvent [70]. Rajabi et al. [70] prepared the silica supported cobalt salen complexes by chemical modification of di-imine cobalt complex using cobalt acetate as a source of cobalt ion (Figure 8). At first Salicylaldehyde was added to the excess amount of absolute MeOH at room temperature and the 3-aminopropyltrimethoxysilane was added to the mixture. The solution turned into yellow color due to the formation of imine which contains a carbon-nitrogen double bond, a hydrogen atom (H), or an organic group is attached to the nitrogen. The addition of cobalt (II) acetate to the imine compound allows the new ligands to complex the cobalt. Prior to surface modification, nanoporous silica was activated by inserting into concentrated HCl and subsequent washing with deionized water (Figure 8).

Rajabi et al. [70] also investigated the catalytic activity of immobilized cobalt catalysts for ethylbenzene oxidation

TABLE 8: Oxidation of ethylbenzene by nickel substituted copper chromite spinels [9].

Catalysts	Conversion (%)	Selectivity (%)		
		Acetophenone	1-phenylethanol	Others
CCr	32.9	13.9	83.4	2.7
CNCr-1	44.7	51.9	46.4	1.7
CNCr-2	56.1	68.7	28.1	3.2
CNCr-3	55.5	55.6	39.6	4.8
NCr	20.2	59.1	19.4	21.5

Reaction conditions: temperature 70°C, time 8 h, EB: TBHP ratio 1 : 2, catalyst weight 0.1 g, solvent 10 mL acetonitrile [9].

TABLE 9: Oxidation reaction of ethylbenzene by reused silica supported Co(II) catalysts.

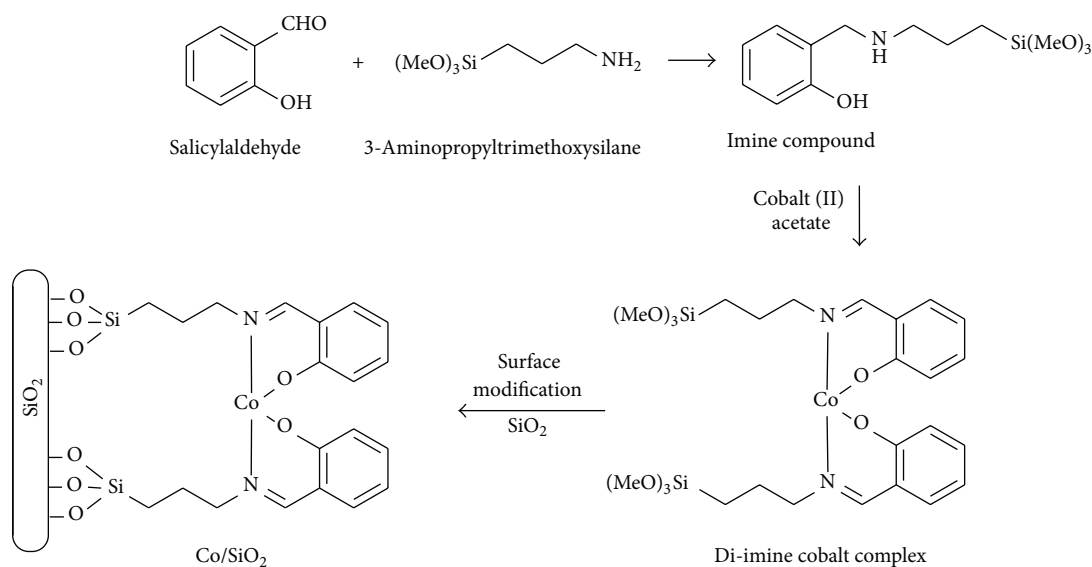| Entry	Run	Temperature (°C)	Selectivity (%)		Yield (%)
			Alcohol	Acetophenone	
1	First	100	9	91	78
2	Second	100	10	90	78
3	Third	100	10	90	77
4	Fourth	100	10	90	70

FIGURE 8: Preparation of silica supported cobalt (II) catalysts by surface chemical modification. Adapted with permission from Elsevier [70].

with O_2 in N-hydroxyphthalimide and other solvents and acetic acid was found to be the best solvent. The selectivity and the conversion rate were increased with temperature. The heterogeneous catalysts were reused four times and a little change in activity was observed (Table 9).

4.6. Nanosized Gold-Catalysts. Materials in nanometer size show properties distinct from their bulk counterparts, because nanosized clusters have electronic structures that have high dense states [71]. Biradar and Asefa (2012) [40] described the oxidation of alkyl substituted benzene over silica supported gold nanoparticles. Supported AuNPs were prepared by *in situ* impregnation method [40] to keep the catalyst well dispersed on the support surfaces. Briefly,

a solution of Pluronic P-123 was added to water and hydrochloric acid. Desired amount of TEOS (tetraethoxysilane) was added to the aqeous acidic Pluronic P-123 solution under stirring. The resulting precipitates was subsequently filtered and washed several time under ambient state to get mesostructured SBA-15. For the synthesis of SBA-15 supported gold catalysts, $HAuCl_4$ solution was made in ethanol/water (1 : 4 ratios) and was well dispersed on the silica support (Figure 9). The lower sized AuNPs demonstrated higher TON (turnover number) and lower TOF (turnover frequency) (Table 10). Solvent effects on oxidation reaction were studied and acetonitrile appeared to be the best solvent. It produced 79% conversion with 93% selectivity towards the ketone products.

TABLE 10: Oxidation of ethylbenzene by three different types of Au/SBA-15 catalysts [40].

Entry	Catalysts/sample (Au average size)	Wt.% (mmol Au/g)	Conversion (%)	Selectivity (%)		TON	TOF (h^{-1})
				Ketone	Alcohol		
1	SBA-15	—	~0	~0	~0	~0	~0
2	Au/SBA-15 catalyst (5.4 ± 1.2 nm)	1.08% (54.8 μmol/g)	68	94	6	764	23
3	Au/SBA-15 catalyst (6.9 ± 1.7 nm)	3.86% (196.0 μmol/g)	79	93	7	274	8
4	Au/SBA-15 catalyst (8.4 ± 2.3 nm)	4.56% (231.5 μmol/g)	89	94	6	256	7

Reaction condition: substrate, ethylbenzene, 1 mmol; oxidant: 80% TBHP (aq.), 2 mmol; solvent: acetonitrile, 10 mL; catalyst: Au/SBA-15 sample with 15 mg overall mass; reaction temperature: 70°C; internal standard: chlorobenzene (0.5 mL); reaction time: 36 h; and reaction atmosphere: air [40].
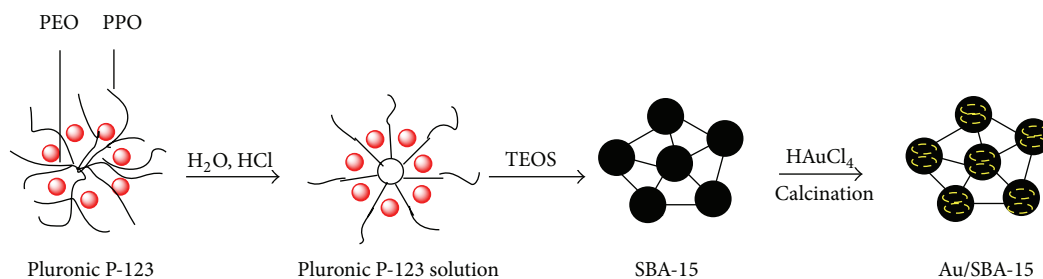

FIGURE 9: Schematic diagram for the synthesis of SBA-15 supported gold catalysts.
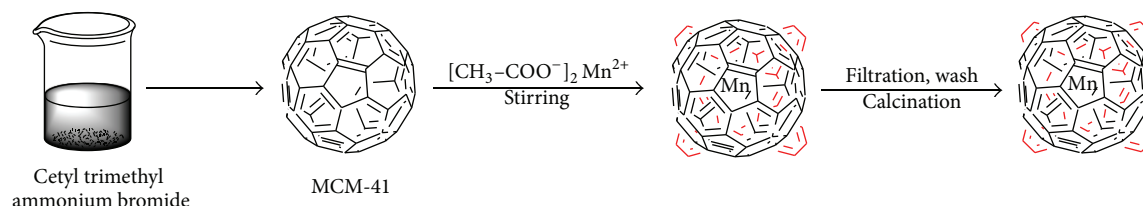

FIGURE 10: Schematic diagram for the synthesis of Mn containing MCM-41 catalysts.

4.7. Mn-Containing MCM-41 Catalyst for the Vapor Phase Oxidation of Alkyl Substituted Benzene. Vapour-phase oxidation of alkyl substituted benzene was performed with carbon dioxide-free air as an oxidant over MnO_2 impregnated MCM-41 catalysts [72]. Vetrivel and Pandurangan [72] synthesized MCM-41 on $C_{16}H_{33}$ $(CH_3)_3N^+Br^-$ template. The Mn containing MCM-41 mesoporous molecular sieves were prepared by impregnating MCM-41 into manganese acetate solutions under stirring overnight. Finally, the solution was filtered, washed, evaporated, and calcined at a specific temperature to obtain Mn containing MCM-41 (Figure 10). They also optimized the reaction conditions by varying reaction temperature, weight hourly space velocity, and time on stream. They carried out a number of reactions with the six types of washed and unwashed Mn containing catalysts. In every case, acetophenone was the major products which increase with the increase of metal content in the catalysts. The high conversion rate to acetophenone was obtained with Mn-MCM-41 catalysts with high Mn content. The unwashed catalysts showed higher reactivity than that of washed one due to the high density of active site in the unwashed catalysts.

5. Preparation Method of Supported Metal Catalysts

A high number of methods have been proposed for the synthesis supported heterogeneous metal catalysts [71]. Table 11 is a summary of the major methods frequently used in catalysts synthesis.

6. Concluding Remark

This review provides an extensive overview of the literature regarding the applications and synthesis of some heterogeneous catalysts for oxidation catalysis. Advantages and disadvantages of certain candidature support materials are presented. Special emphasis is given to heterogeneous catalysis, specially the metal-support synergy. The role of appropriate solvent that codissolves the catalysts and substrate to ease the pretreatment and oxidation process is tabulated for better understanding. In line with the goal of industrial process, reaction conditioning and utilization of appropriate and cheap catalysts are briefly outlined. Future research should

TABLE 11: Major methods of catalysts synthesis.

Method	Brief description	Limitations	References
Deposition-precipitation	(a) Deposition-precipitation method is easier for the synthesis of various supported metal catalyst complexes in presence of excess alkali. (b) In alkaline media the $[Au(en)_2]_3$ + cations are deposited on anionic oxide (TiO_2, Fe_2O_3, Al_2O_3, ZrO_2, and CeO_2) surfaces having high isoelectric point (PI > 7.00). (c) Functionalization of oxides may take part in the reaction as co-catalysts for the enhancement of the catalytic activity. (d) It is a very good method for the oxidation of alkanes to epoxides.	(a) It is a multistep processes for the deposition of metal onto the oxide surface. (b) It cannot integrate AuNPs on metal oxides of low isoelectric point (IEP ~2) such as SiO_2. (c) It is limited to maximum 1 wt% Au-loading. (d) It requires multiple washing steps to eliminate excess chloride	[40, 136, 137]
Cocondensation	(a) It simultaneously forms mesostructure to anchor gold. (b) It easily forms hexagonal array of mesopores and metal crystallites of 3–18 nm in diameter. (c) It is a simple method to insert gold nanoparticles onto the surface of oxides. (d) It permits the formation of particles in metallic state surrounded by chloride ions. These Cl⁻ ions are the basic species for catalysts activation during acetonylacetone (AcAc) transformation (cyclization/dehydration) in gaseous state and also act as promoters for electron transfer to O_2 during NO reduction with propene in presence of oxygen.	(a) The surface area of catalysts, prepared by this method, is low.	[136, 138]
Anion adsorption	(a) Aqueous anions (sulfate, arsenates, and anionic functional groups of biomolecules) are adsorbed on the electrically charged metal oxide surfaces (b) Optimum gold loading takes place at 80°C. (c) It is a simple method, with no need for expensive instrumentations and expert personnel.	(a) Gold loading cannot exceed 1.5 wt%. (b) It requires multiple washing steps.	[137, 139, 140]
Cation adsorption	(a) Catalyst can be prepared at room temperature to avoid decomposition of the metal complex and reduction of gold. (b) Higher loading of gold (3 wt%) can be achieved and cation adsorption with metal leads to smaller particles (~2 nm) when the solution/support contact time is moderate (1h)	(a) In general, the Au loading did not exceed 2 wt%.	[139, 141]

Table 11: Continued.

Method	Brief description	Limitations	References
Incipient wetness impregnation	(a) Interaction of gold precursors and the support surface takes place between the oxygen atoms of Me_2Au (acetonylacetone) and the OH groups of the SiO_2 surface at high temperature ($\sim$300°C). (b) Strong interaction between the metal catalyst and support oxides. Thus catalyst is not easily lost.	(a) The chlorides on support promote the aggregation of AuNPs and frequently poison the active sites of the catalyst. (b) Low pH (<1) and high temperature are prerequisite (>300°C). Contains higher amount of chloride impurities. (c) It cannot produce homogeneous and stable particles.	[136, 137, 139]
Dispersion	(a) it is an attractive method to control the aggregation of AuNPs. (b) Particle size is preserved during the immobilization step. (c) Particles size can easily be controlled. (d) It is highly selective and efficient.	(a) It requires extensive washing steps to remove excess chloride impurities.	[40, 136]
Chemical vapor deposition	(a) Supports are evacuated in vacuum at 200°C for 4 h to remove the adsorbed water (b) In general, OMCVD method involved in a system where the proportion between the substrate area and gas phase volume gets larger, so that the surface reactions hold a key parameter.	(a) It is expensive, requires special equipment, and the amount of metal incorporated by this method is somehow limited by pore volume of inert solid support.	[142, 143]
Etching	(a) It is synthetic methods for yolk-shell nanoparticles (b) It is efficient, cheaper and simple method	(a) Catalysts work only at low temperature.	[40, 144]

focus on the synthesis and application of more efficient heterogeneous catalysts as well as synergizing the catalyst cost for large scale synthesis.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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