Review Article

Recent Development of Catalytic Materials for Ethylbenzene Oxidation

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Catalysts are well-known to convert alkylbenzenes at high thermal condition to a number of useful products. However, the current schemes of transformation are not suitable for the hazard-free industrial applications because their reactive intermediates are transformed to a variety of side products that often retard the optimum yield and cause environmental pollutions. It is also observed that the formation of products depends on a wide range of parameters which are extremely difficult to control and often incur extra cost. Recently, heterogeneous catalysts have received huge commercial interests for the oxidation of alkylbenzene into carbonyl compounds which are platform chemicals in various synthetics and fine chemicals. This review is an up-to-date documentary on various catalysts used for the oxidation of alkyl-substituted benzenes along with their reaction condition and selectivity profiles. This work updates our knowledge for the selection and/or design of novel catalysts for the chemists and engineers in the industrial and academic settings.

1. Introduction

The oxidations of hydrocarbons to its corresponding carbonyl group (aldehydes or ketones) have a substantial value in organic synthesis, both in laboratory and in industry [1, 2]. It is remarkable to note that the global production of carbonyl composites per year has exceeded 10^7 tones and many of these are produced from the direct oxidation of hydrocarbons [3]. In this regard, the catalyst-assisted oxidation processes have made significant contributions in the production of various chemicals, cosmetics, drugs, and other useful compounds. Among the various substrates used in oxidation reactions, aryl alkanes, such as ethylbenzene, have huge interests because

their essential oxidation products are a rich source of a number of drugs and synthetics. For example, the oxidation products of ethylbenzene such as acetophenone and 1-phenylethanol are the precursors of optically active alcohols [4], benzalacetophenones (chalcones) [5, 6], and hydrazones [7].

The oxidation process was traditionally carried out by a stoichiometric amount of oxidants such as permanganates [8, 9], chromium reagents [10–13], ruthenium (VIII) oxide [14, 15], activated dimethyl sulfoxide (DMSO) [16] or Dess–Martin periodinane [17], and TPAP/NMO (*tetra-N-propylammonium perruthenate/N-methyl-morpholine-N-oxide*) [18], and all these involve high temperature and/or pressure and corrosive and toxic chemicals and produce

FIGURE 1: Major approaches to alkylbenzene oxidation.

an equivalent amount of waste metals, incurring the environmental burden such as halogenated organic solvents (hydrocarbons) [19, 20]. On the other hand, noncatalytic transformation under supercritical conditions [21] is immature and unsuitable commercial application due to the lack of stability and selectivity (Figure 1).

Therefore, the catalytic approaches which offer low temperature and more selective conversion, minimizing the uses and/or formation of undesirable byproducts, have evolved as the method of choice for hydrocarbon oxidation using air or clean molecular oxygen (O_2) as oxygen source (Scheme 1) [21]. Hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (TBHP) could also be used as oxygen source due to its obvious advantages in oxidation reaction [22, 23]. The aim of this review is to provide a brief but comprehensive outline of the major catalytic approaches for alkylbenzene oxidation along with some other oxidation reactions.

2. Nanotechnology for Ethylbenzene Oxidation

Nanotechnology has set immeasurable status in the oxidation of ethylbenzene. Various catalytic materials with high surface area, high surface to volume ratio, reactivity, tunable pore size, and hydrophilic and hydrophobic interfaces are promising in catalysis. Several nanometals, such as gold [23], copper [24], titanium [25], silver [26], nickel [27], manganese [28], cobalt [29] and tin [25], deposited on solid supports are suitable in oxidation reaction. Functionalized silica with homogeneous metal dispersion which prevents metal agglomeration is efficient in ethylbenzene oxidation [23]. Gold-mediated ethylbenzene oxidation perhaps initiates Au nanoparticle-based decomposition of reactive oxidant to oxidant radical species followed by two different oxidation reactions, forming ketones and secondary alcohols [23]. Moreover, nanomaterials have increased sur-

SCHEME 1: Catalytic schemes for the aerobic oxidation of ethylbenzene.

face porosity that uses low free energy for the reaction to happen [30]. Nanoparticles oxidize not only ethylbenzene but also various alkanes with improved catalysis [31]. In addition, nanoparticles can activate reaction as bimetallic forms with several other metals and metal oxide with controllable shape and composition. Even though nanomaterials are appreciated in oxidation reaction, they have some limitations. Thermal instability, high-pressure requirement, metal agglomeration, pore blocking, slow reaction, poor conversion and selectivity, and the formation of side products are frequent matters in this perspective. Poor recyclability and hidden hazards to ecosystems are also leading concerns [32]. Therefore, a consistent, nontoxic, delicate, and economical oxidation process has become the most laborious task in ethylbenzene oxidation.

3. Catalytic Method

The major goal of using a catalyst is to speed up or accelerate the rate of a chemical reaction. It remains unchanged at the end of the reaction but minimizes the activation/free energy that is needed to attain the transition state while keeping

the total free energy of the reactants and products unchanged in the course of the reaction [33, 34]. The major catalytic processes for alkylbenzene oxidation are briefly presented step-by-step.

3.1. Homogeneous Catalysis. Homogeneous catalysts are those which exist in the same phase with the reactants and products; the catalysts fully dissolve in the reaction medium exposing all the catalytic sites to interact with the substrates. Homogeneous catalysts are usually complexes, often consisting of a metal which is bound to several organic ligands. The ligands are responsible for providing the stability as well as the solubility of the catalyst complex metal, and they could be adjusted to enhance selectivity of a catalyst towards the synthesis of a specific desirable product [35]. The great achievement of a homogeneous catalyst is that it can make a product with >90% selectivity at a high conversion rate through the careful selection of the metal center, ligands, reaction parameters, and a suitable substrate [31]. Although there are widespread advantages of selectivity in homogeneous catalysis, scientists are paying enormous attention to heterogeneous catalysts; this is due to the difficulty in the separation of homogeneous catalysts. Homogeneous catalysts are also known to cause corrosion to the reaction vessels, and some of them are deposited onto the reactor wall. Thus, the workup procedure for homogeneous catalysts is not straightforward (Figure 1) [36]. Here, we represent some homogeneous catalysts used in alkylbenzene oxidation with conversion and selectivity to acetophenone (Table 1).

3.2. Heterogeneous Catalysis. Heterogeneous catalysts are those which exist in different phase from the reactants and products. They offer several advantages over their homogeneous counterparts in terms of separation and recyclability [31, 44]. These catalysts are usually solid, but the reactants could be either solid or liquid; so they could be easily detached from the reaction mixture by simple centrifugation and washing, keeping the manufacturing cost at the minimal level. 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. Consequently, scientists have drawn huge attention as the oxidation catalyst for alkylbenzene conversion with better conversion rate and higher selectivity towards ketone products which are essential intermediates for the synthesis of many specialty chemicals with high economic value such as agrochemicals, pharmaceuticals, and perfumes [45]. Herein, we describe some representative heterogeneous catalysts on various supports for ethylbenzene oxidation.

3.2.1. Nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ Support. Recently, the nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ support is used for the synthesis of various metal complexes such as Mn [28, 45, 46], Fe [47], and Co [29, 48, 49] catalysts for catalytic oxidation of ethylbenzene (Table 3). Arshadi and Ghiaci [44] synthesized nanosized $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed oxide supports and functionalized it with 3-aminopropyl-triethoxysilane (3-APTES) and 2-ami-

noethyl-3-aminopropyltrimethoxysilane (2-AE-3-APTMS) linkers (Figure 2). Thus, functionalized oxide was further functionalized with Schiff base by conjugating it to $\text{Mn}(\text{OAc})_2$ to fabricate immobilized Mn catalyst complex. This heterogeneous Mn catalysts exhibited 67% ethylbenzene conversion along with 93% selectivity towards acetophenone at 80°C using TBHP (*tert*-butyl hydroperoxide) as an oxidant in the absence of any solvent. Arshadi et al. [29] further prepared Cobalt(II) Schiff base complexes immobilized onto $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed oxide supports combining two diverse linkers, 3-APTES and 2-AE-3-APTMS (Figure 2). This heterogeneous Cobalt(II) complexes resulted in 86% conversion of ethylbenzene with 99% selectivity toward acetophenone.

In 2012, Arshadi et al. [46] synthesized Mn catalysts on modified $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed oxide supports using 2-AE-3-APTMS (Figure 3); this performed oxidation under mild conditions with a lower oxidation potential and charge-transfer resistance but leads to a greater conversion (91%) and better selectivity (98%) in the presence of supercritical carbon dioxide under solvent-free atmosphere. The catalysts were reused for eight times with a minimum loss of activity. In another instance, Habibi and Faraji [28] synthesized heterogeneous Mn nanocatalysts anchored on $\text{SiO}_2\text{-Al}_2\text{O}_3$ hybrid supports using a bidentate ligand of nitrogen atoms (Figure 3). The catalysts showed remarkable activity in the oxidation of ethylbenzene (conversion rate 67% and selectivity 84%) in the absence of any chemical solvent. On the other hand, Co(II) nanocatalyst was prepared by attaching of cobalt ions on inert bipyridylketone over the nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixed oxides (Figure 3) [49]. The catalytic oxidations of the prepared nanocatalyst towards ethylbenzene were assessed with TBHP as an oxidant in the absence of any solvent. Under optimal conditions, the nanocatalyst showed 79% selectivity towards the acetophenone with 47.2% conversion. Habibi and coworkers prepared another catalyst by immobilizing cobalt ion on $\text{SiO}_2\text{-Al}_2\text{O}_3$ support (Figure 3) [48]. This performed ethylbenzene oxidation in *N*-hydroxyphthalimide (2-hydroxy-1*H*-isoindole-1,3-dione (NHPI)) with 82% selectivity in an oxygen atmosphere and acetic acid solvent at 100°C. Very recently, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-APTMS-BPK-Mn(III)}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-APTMS-BPK-Co(II)}$ catalysts were synthesized (Figure 3); these carried out the ethylbenzene oxidation in NHPI without using any reducing agent under an oxygen atmosphere. Conversion rates were 53% and 81% with selectivities 74% and 98% towards acetophenone, respectively [45].

A novel and very simple Fe nanocatalyst on a modified nanoscale $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Figure 4) was studied for alkylbenzene oxidation [47]. Under optimal environments (substrate to the TBHP ratio (1:1), in the absence of solvent, at 50-120°C and 24 h reaction time), an Fe nanocatalyst exhibited 40% conversion and 89% selectivity.

3.2.2. Silica (SiO_2) Support. Silica has achieved a great interest for many catalysts; this is due to their three-dimensional open-pore network structures, high surface to volume ratio, high reusability, and distinct optoelectronic and physiochemical properties; these provide well dispersion of metal

TABLE 1: Homogeneous catalysts in ethylbenzene oxidation.

Catalysts	Oxidant	Reaction conditions Solvent	Temperature (°C)	Reaction time (hour)	Major products	Conversion (%)	Selectivity (%)	Ref.
1-Glycyl-3-methyl imidazolium chloride-copper (II) complex	2 mmol NaClO	Solvent free	25	10	Acetophenone	85	85	[37]
CrO ₃ /CeSO ₄	H ₅ IO ₆	Acetonitrile	30	1	Acetophenone	100	49	[38]
CrO ₃	Ce(SO ₄) ₂	Acetic acid	50	5	Acetophenone	100	61	[39]
1,4-dichloro-1,4-diazoniabicyclo [2] octane bis-chloride	—	Water	40	10	Acetophenone	—	95	[40]
Mixed valent dirhodium(II,III) tetrakis(caprolactamate)	TBHP and dichloroethane	—	40	16	Acetophenone	42	20	[41]
48% HBr & 30% H ₂ O ₂	H ₂ O ₂	Dichloromethane	30	12	Acetophenone	95	75	[42]
Cobalt(II) phthalocyanine	Oxygen	Ionic liquid 1-butyl-3-methyl- imidazoliumbromide	100	7	Acetophenone	—	77	[43]

TABLE 2: Recently used heterogeneous catalysts in oxidation reactions.

Year	Catalysts	Method of catalysts synthesis	Application	Ref.
2019	Mn catalysts on various supports	Coprecipitation	Carbon monoxide oxidation	[50]
	Copper promoted ceria	Hydrothermal	Carbon monoxide oxidation	[51]
	Copper on titania aerogel	Wet impregnation	Carbon monoxide oxidation	[52]
	Pd supported on CeO ₂ (100) and CeO ₂ (111) facets	Hydrothermal	Carbon monoxide oxidation	[53]
	Copper on titania hollow sphere	Wet chemical	Methanol oxidation	[54]
	Pt-based catalysts	Chemical reduction	Glycerol	[55]
	RuO ₂ /TiO ₂ catalyst	—	Hg ⁰ oxidation	[56]
2018	MnO ₂ hollow sphere	Precipitation	Formaldehyde oxidation	[57]
	Ruthenium catalyst	—	Water oxidation	[58]
	Solid catalyst on various supports	Impregnation	1-Octanol oxidation	[59]
	Bioinspired manganese catalysts	—	Enantioselective oxidation of spirocyclic compounds	[60]
	Pt catalyst on carbon	—	Xylose	[61]
	α -ZrP, Mn(II)	Ion exchange	Cyclohexane oxidation	[62]
2017	Pt-Sn on carbon support	Formic acid reduction	Ethanol and carbon monoxide oxidation	[63]
	Pt-Ru/C	Colloidal method	Glycerol oxidation	[64]
	Porphyritic metal-organic framework	Postsynthetic modification	Cyclohexane	[65]
	MnO _x -CeO ₂ supported on Co-N-C	Coprecipitation	Ethylbenzene oxidation	[66]
	Pd-Pt nanocubes	Wet impregnation	Carbon monoxide oxidation	[67]
	Pt ₃ Ni alloy nanoparticles	Impregnation	Carbon monoxide oxidation	[68]
2016	Boron-doped crystalline diamond	—	Aliphatic polyamine oxidation	[69]
	Pd/graphene	Sonochemical and chemical-reduction	Glucose oxidation	[70]
	PdO/graphene	Cyclic voltammetry (CV) and chronoamperometry (CA)	Ethanol oxidation	[71]
	Graphene-supported palladium	—	Formaldehyde oxidation	[72]
2015	PtAg bimetallic alloy	Coreduction	Methanol oxidation	[73]
	Pt/carbon xerogel and Vulcan carbon	Impregnation, microemulsion	Methanol oxidation	[74]
	Nickel supported on nitrogen-doped carbon nanotubes	Hydrothermal	Hydrogen oxidation	[27]
	Lanthanum-based perovskite supports for AuPt nanoparticles	SAS precipitation	Glycerol oxidation	[75]

TABLE 2: Continued.

Year	Catalysts	Method of catalysts synthesis	Application	Ref.
2014	Au/MnO	Photochemical, electrochemical	Water oxidation	[76]
	Pd-Cu nanoalloy	Soft chemical method	Methanol oxidation	[77]
	Cu (II) functionalized Fe ₃ O ₄	—	Sulfides and thiols	[78]
	Pd-Cu bimetal	Coreduection	Ethanol oxidation	[79]
2013	Pd nanohollow/Pt nanorod core/shell composite	Multistep crystalline growth	Methanol oxidation	[80]
	Au/Mg(OH) ₂	Deposition	Carbon monoxide	[81]
	Au/Al ₂ O ₃ , Au/C	Dispersion	Glucose oxidation	[82]
	Au/Pt bimetallic nanoparticles	Dispersion, reduction	Glucose oxidation	[83]
2012	Au/CuO	Coprecipitation	Carbon monoxide	[84]
	Au/C	Incipient wet impregnation	Glucose oxidation	[85]
	Au/SiO ₂	Stöber method	Cyclohexene and d-glucose oxidation	[86]
	Au-Cu/SiO ₂	Two-step method	Alcohol	[87]
2011	Au-Pd/MgO	Sol immobilization, adsorption-reduction	Benzyl alcohol oxidation	[88]
	Pd-Ni electrocatalysts	Nanocapsule	Ethanol oxidation	[89]
	PtBi/C electrocatalysts	Borohydride reduction	Ethanol electrooxidation	[90]
	PdIr/C	Simultaneous reduction	Ethanol oxidation	[91]
2010	PtSn/C-Rh, PtSn/C-CeO	Alcohol reduction, polymeric precursor	Ethanol oxidation	[92]
	Gold nanoparticles	Reduction	Glucose and 1-phenyl ethanol	[93]
	Supported gold nanoparticles	—	Silanol oxidation	[94]
	Metalloporphyrin and cobalt acetate	Condensation	<i>p</i> -Xylene oxidation	[95]
2009	Au/TiO ₂	Deposition precipitation	Alcohol oxidation	[96]
	Gold catalysts	—	Alcohol oxidation	[97]
	CuO/mesoporous silica	Impregnation	Benzene oxidation	[98]
	Supported gold catalysts	Deposition precipitation	Alcohol oxidation	[99]
2005	Gold with anionic ligand	Precipitation	Alcohol oxidation	[100]

TABLE 3: Oxidation of alkylbenzene by $\text{SiO}_2/\text{Al}_2\text{O}_3$ supports.

Name of catalysts	Substrate	Oxidant	Reaction time (h)	Reaction temperature ($^{\circ}\text{C}$)/solvent	Conversion (%)	Selectivity (%)	Ref.
$\text{SiO}_2/\text{Al}_2\text{O}_3$ -APTMS-BPK-Mn, NHPI		O_2	8	100/acetic acid	53	74	[45]
$\text{SiO}_2/\text{Al}_2\text{O}_3$ -APTMS-BPK-Co(II), NHPI		O_2	8	100/acetic acid	81	98	[45]
Nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ supported cobalt, NHPI		O_2	8	100/acetic acid	64	82	[48]
Nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ modified Fe nanocatalysts		TBHP	24	50/solvent free	40	89	[47]
Nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$ supported cobalt	Ethylbenzene	TBHP	24	100/solvent free	47	79	[49]
Mn nanocatalysts modified on nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$		TBHP	24	100/solvent free	67	84	[28]
SiO_2 - Al_2O_3 mixed oxide immobilized Mn catalysts		TBHP	24	80/solvent free	67	93	[44]
SiO_2 - Al_2O_3 mixed oxide immobilized cobalt catalysts		TBHP	24	80/solvent free	86	99	[29]
Mn supported on SiO_2 - Al_2O_3 , scCO_2		TBHP	24	120/ CO_2	86	88	[46]

NHPI = N-hydroxyphthalimide; BPK = bipyridylketone; APTMS = trimethoxysilylpropylamine; SC = supercritical.

FIGURE 2: Immobilization of metal (Mn/Co) ion onto functionalized $\text{SiO}_2/\text{Al}_2\text{O}_3$ using linker molecule. Adapted with permission from Elsevier [29, 44].

nanoparticles and facilitate the transport of molecules, ions, or electrons through the nanopores/nanochannels, enhancing product yields with minimum cost and time. Mal and Ramaswamy [25] reported the synthesis and catalytic activity of three different metals (Ti, V, or Sn) on silica supports (a new hydrophobic crystalline silica molecular sieve) using hydrogen peroxide as an oxidant at 60–80°C [101]. Of the three metallosilicates, Sn-silicalite-I was very reactive with H_2O_2 , accounting for 60% catalytic efficiency. On the other hand, TS-1 (Si/Ti) and VS-1 (Si/V) demonstrated only 36.2% and 20.10% conversion, respectively. These catalysts oxidize ethylbenzene in two different ways: first, by hydroxylating of arene at *para*-position and some extending to *ortho*-position and, second, by adding oxygen at the side chain of primary and secondary (α - and β -) carbon atom; the corre-

sponding carbinols (primary/secondary), which result from the side chain oxidation, further undergo to yield aldehyde or ketone. Normally, the oxidation at β -carbon dominates over the α -carbon. In case of TS-1, the oxidation does not occur at α -carbon. On the other hand, both positions are oxidized by VS-1 and Sn-silicalite-1. These hydroxylation reactions proceed an ionic mechanism onto TS-1 and TS-2 surfaces [102, 103]. Nonetheless, the product distribution reveals that the side chain product is almost 4 to 5 times higher than that of aromatic ring oxidation. Ghiaci et al. [104] immobilized Mn(III) porphyrin complexes $[\text{Mn}(\text{TMCP})][\text{TMCP}:\text{5,10,15,20-tetrakis-(4-methoxycarbonylphenyl)-porphyrin}]$ onto organo-functionalized silica gel (Figure 5). This catalyst results in 40.8% conversion but 96.6% selectivity in the liquid phase oxidation of

FIGURE 3: Synthetic process of Si/Al-APTMS-BPK-Mn/Co catalyst. Adapted with permission from Elsevier [28, 48].

FIGURE 4: Immobilization of Fe on nanohybrid $\text{SiO}_2/\text{Al}_2\text{O}_3$. Adapted with permission from Elsevier [47].

ethylbenzene using TBPH as oxidant and without any solvent at 150°C . They further tested the effect of reaction time and found the catalysts exhibit maximum activity in 24 hours.

On the other hand, Rajabi and his colleagues [105] successfully prepared and employed silica supported Cobalt(II) salen complex (Figure 6); cobalt acetate was used as a source of Cobalt(II) ion, for the aerobic oxidation of ethylbenzene in presence NHPI at atmospheric pressure. The catalysts were recycled for at least four times, and in the first cycle, 78% product yield and 91% selectivity were realized.

Biradar and Asefa [23] have stated the preparation method of gold nanoparticles as efficient catalysts for alkylbenzene oxidation by reducing Au(III) ions onto mesoporous silica functionalized by hemiaminal reducing agents (Figure 7). The supported nanoporous gold demonstrated efficient catalytic action for the oxidation of diverse range alkyl benzenes as well as linear alkanes in the presence of a TBHP oxidant. It provided unprecedented conversion ($\sim 99\%$) and selectivity ($\sim 100\%$) toward carbonyl ketones under mild conditions. They also found that the mesoporous silica supported gold nanocatalysts exhibit the highest activity for ethylbenzene oxidation in acetonitrile followed by THF, ethyl acetate, and toluene, showing that the polar solvents have positive impact on polarity and/or dielectric con-

stant of the reaction intermediates. Moreover, certain solvents outperform others by undergoing a cooxidation process which results in a more powerful oxidizing agent in the course of the reaction.

Anand et al. [26] synthesized four different types of crystalline Ag nanoparticles by impregnating silica with aqueous silver nitrate (Figure 7) and subsequent evaporation at 100°C . The crystalline Ag nanoparticles of size 37 nm showed maximum conversion (92%) and selectivity (99%) towards acetophenone in the absence of any solvent at 90°C . Cobalt(II) Schiff base complexes with modified silica were prepared by refluxing silica gel with 3-aminopropyl-trimethoxysilane in dry dichloromethane wherein the silica was liganded with $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ [106]. The catalysts exhibited 98% conversion and 99% selectivity towards ketone products in the presence of NHPI under an O_2 atmosphere. Neeli et al. [24] prepared Cu/SBA-15 catalysts by loading Cu via impregnation wherein $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is the metal source (Figure 7). At 10% Cu loading, the maximum conversion (94%) and selectivity (99%) to acetophenone under solvent-free condition were achieved at 90°C .

In another instance, Dan-Hua et al. [36] immobilized manganese porphyrin onto silica nanoparticles on Fe_3O_4 solid matrixes. The catalysts become active upon the removal of the hard template of the silica supports.

FIGURE 5: Metalloporphyrin metal ion covalently bound to silica. Adapted with permission from Elsevier [104].

FIGURE 6: Preparation of silica supported Cobalt(II) catalyst. Adapted with permission from Elsevier [105].

Metalloporphyrin was fixed onto the inner surface of hollow microspheres allowing a substrate to diffuse onto grafted manganese porphyrin through the pore of the silica shell. The catalysts were recycled for six times with the retention of high activity and stability. Bhoware et al. [107] prepared cobalt nanocatalysts onto hexagonal mesoporous materials (Co-HMS and Co/HMS) by grafting various cobalt contents via hydrothermal and postsynthesis methods. The catalysts exhibited good activity for liquid-phase ethylbenzene oxidation in the presence of the TBHP

oxidant wherein H_2O_2 was inactive under solvent-free condition accounting for 49.5% and 39.0% by Co-HMS and Co/HMS, respectively, in a 24-hour reaction at 80°C; Co/HMS catalysts exhibited greater selectivity (59%) towards acetophenone. Sujandi et al. [108] immobilized Co(III) ion onto cyclam (macrocyclic ring, Scheme 2) complexed to functionalized SBA-15 with a chloropropyl group through surface substitution reaction. This cyclam group deposits Cobalt(II) into its cavity that facilitates ethylbenzene oxidation with better conversion efficiency

FIGURE 7: General procedure for the synthesis of silica-supported metal catalysts.

Cyclam ring

SCHEME 2

(60%). The presence of a pyridine group to the axial site of Co(III) cyclam composite was further investigated, conferring that this group enhances the ethylbenzene conversion by 10% without losing the selectivity towards acetophenone. Major silica-based catalysts for ethylbenzene oxidation are summarized in Table 4.

3.2.3. Miscellaneous. Apart from these, a good number of catalysts are being used for ethylbenzene oxidation (Table 5). Rebelo et al. [110] synthesized and studied the activity of five different types of Mn(III) porphyrin complexes in ammonium acetate as cocatalysts. Among these, Mn(β -NO₂TDCPP)Cl provided the highest conversion and selectivity due to the presence of a nitro group. The cocatalysts for hydrogen peroxide activation included the buffering substances, i.e., ammonium acetate [111], imidazole [112], and pyridine plus benzoic acid [113]. However, the evidence of pyridine oxidation was also observed [114]. Xavier et al. [115] reported Y-zeolite supported Co(II), Ni(II), and Cu(II) centers of dimethylglyoxime and *N,N'*-ethylenebis (7-methylsalicylideneamine) which were prepared in situ by reaction of ion-exchanged metal ions with disulfide flexible ligands. However, Cu(II)-zeolite complexes demonstrated maximum efficiency wherein the reactivity of the complex is believed to be provided by the geometry of encapsulated molecules as well as the steric condition of active sites. The supported zeolite composites are highly stationary to be recycled and are apt to be used as catalysts for partial oxidation. Choudhary et al. [116] investigated the cat-

alytic effect of MnO₄⁻¹-exchanged Mg-Al hydrotalcite which is a stable and green catalyst for the oxidation of a methylene group, covalently attached to an aromatic ring under an oxygen atmosphere. They found that the activity of methylene-to-carbonyl conversion by MnO₄⁻¹-exchanged hydrotalcite, the decomposition of H₂O₂, and the basicity of Mg-Al hydrotalcite rises with the raising Mg/Al ratio in the catalyst and the Mg/Al ratio at 10; the highest catalytic activity as well as selectivity (above 95%) was obtained for ethylbenzene oxidation to acetophenone and diphenylmethane to benzophenone. These reactions were fully heterogeneous, but no leaching of the active component(s) from the catalyst was observed. The recycled catalyst exhibited good performance after its first use in the oxidation reaction.

Bennur et al. [117] synthesized copper *tri*- and *tetra*-aza macrocyclic complexes by encapsulating Y-type zeolite. The “neat” and encapsulated complexes showed noble performance in ethylbenzene oxidation at 60°C using TBHP as an oxidant. While the encapsulated complexes showed enhanced selectivity towards acetophenone, a small quantity of *o*- and *p*-hydroxyacetophenones was also yielded, reflecting that C-H bond activation takes place both at benzylic and at aromatic ring carbon atoms. It is inferred that ring hydroxylation takes place more over the “neat” complexes than over the encapsulated complexes. This difference is due to the formation of various types of “active” copper-oxygen intermediates, such as bis- μ -oxo complexes and Cu-hydroperoxo species, at different proportions over the “neat” and encapsulated complexes. In 2006, Jana et al. [118] prepared different NiAl hydrotalcites by a conventional precipitation technique using Ni/Al at molar ratios of 2-5 in guest inorganic anions such as CO₃²⁻ and Cl⁻; these carried out the liquid-phase oxidation of the methylene group of ethyl-substituted benzene to acetophenone under an atmospheric oxygen as the sole oxidant in a solvent-free system at 135°C. In the presence of CO₃²⁻ anion and Ni/Al ratio 5 mol mol⁻¹, it showed higher activity for ethylbenzene oxidation with 99% selectivity towards acetophenone than those prepared using Cl⁻, NO₃⁻, or SO₄²⁻ anions. Other hydrotalcite congaing transition-metal solid catalysts such as CuAl-, ZnAl-, CoAl-, MgFe-, and MgCr- demonstrated higher activity than that of NiAl hydrotalcite. However, the active NiAl hydrotalcite presented

TABLE 4: Oxidation of alkylbenzene by SiO₂ supports.

Name of catalysts	Substrate	Oxidant	Reaction time (h)	Reaction temperature (°C)/solvent	Conversion (%)	Selectivity (%)	Ref.
Ti, V & Sn containing silicalite molecular sieves	Ethylbenzene	H ₂ O ₂	24	80/ <i>tert</i> -butanol, acetone, water	—	—	[25]
Silica gel supported cobalt, NHPI		O ₂	24	100/acetic acid	98	99	[106]
Cu/SBA-15		TBHP	5	90/solvent free	94	99	[24]
Metalloporphyrin@SiO ₂		O ₂	—	100/solvent free	16	74	[36]
Ag/SBA-15		TBHP	5	90/solvent free	92	99	[26]
Au/SBA-15		TBHP	36	70/acetonitrile	79	93	[23]
Silica supported cobalt, NHPI		O ₂	<12	100/acetic acid	78	91	[105]
SF-ATPS-Mn(III)TMCPP		TBHP	24	150/solvent free	40	96	[104]
CO/HMS		TBHP	24	80/solvent free	49	60	[107]
Co (III) cyclam functionalized mesoporous silica		Air flow	8	-/acetonitrile	20	60	[108]
Mn-metformin complex on modified magnetic SiO ₂ @Fe ₃ O ₄ core/shell		O ₂	8	100/acetic acid	85	98	[109]

TMCPP: 5,10,15,20-tetrakis(4-methoxy carbonyl phenyl) porphyrin; AMTS = aminopropyl-trimethoxysilane.

TABLE 5: Oxidation of ethylbenzene with various catalytic supports materials.

Name of catalysts	Substrate	Oxidant	Reaction time (h)	Reaction temperature (°C)/solvent	Conversion (%)	Selectivity (%)	Ref.
Manganese (III) porphyrin, ammonium acetate	Ethylbenzene	H ₂ O ₂	5.5	Room temperature/acetonitrile	66	66	[110]
Zeolite-encapsulated Cu (II)			8	70/benzene	46	66	[115]
MnO 4-1 exchanged Mg-Al hydrotalcite			5	-/solvent free	22	98	[116]
Cu(tacn)(ClO ₄) ₂			10	60/acetonitrile	49	91	[117]
Ni/Al hydrotalcites, CO ₃ ²⁻			5	135/solvent free	47	99	[118]
Vanadia/ceria			6	60/acetonitrile	20	72	[119]
Cobalt(II)(5,10,15,20-tetrakis (pentafluorophenyl))porphyrin			24	100/solvent free	38	94	[120]
Hemin/NHPI			9	100/acetonitrile	92	94	[121]
Supported nickel			5	150/solvent free	20	80	[122]
Metal-doped HS-ALF ₃			6	60/acetonitrile	70	72	[125]
Macrocyclic copper (II) complex			10	60/acetonitrile	62	88	[126]
DAEP-bentonite-Pd (II)			24	80/solvent free	92	93	[127]
Ni substituted copper chromite spinel			8	70/acetonitrile	56	68	[128]
Vanadium complex/NHPI system			12	90/Benzonitrile	69	97	[142]
Mesoporous Cu-ZrPO			24	80/Benzonitrile	91	87	[145]
Immobilized bidentate Schiff base oxovanadium(IV) complex			14	110/solvent free	~40	98	[143]
Fe@CNT			3	155/acetonitrile	36	60	[144]
Supported Co ₄ HP ₂ Mo ₁₅ V ₃ O ₆₂			—	70/glacial acetic acid	72	95	[146]
μ-Oxo dimeric metalloporphyrins			2	65/solvent free	91	99	[147]
Cobalt-supported catalysts on modified MNPs			10	100/ethanol	88	98	[148]
Carbon nanotube			4	155/acetonitrile	40	62	[149]
Mn/N-C/Al ₂ O ₃			6	120/solvent free	27	99	[150]
Mesosubstituted pyrazolyl porphyrin complexes				80/water	99	99	[151]

Tacn = triazacyclononane; HMS = hexagonal mesoporous materials; MNPs = magnetic nanoparticles.

better performance in the oxidation of a variety of alkylaromatics to their corresponding benzylic ketones under similar reaction conditions. Additionally, the preparation of NiAl hydrotalcite is very cheap and stable using commercially available reagents.

Radhika and Sugunan [119] impregnated ammonium metavanadate in oxalic acid solution to prepare vanadia/ceria catalysts (2-10% of V_2O_5) and carried out liquid-phase oxidation of ethylbenzene with H_2O_2 . It was found that the activity was increased with loading of V_2O_5 up to 8%; however, it decreased after V_2O_5 content (10%). In some instances, catalytic activity increases even after vanadia loading beyond 10%, but selectivity towards acetophenone decreases. Product analysis indicated that when vanadia loading higher than 6%, it oxidizes the acetophenone to 2-hydroxyacetophenone. XRD and FT-IR analysis revealed the existence of extremely dispersed vanadia at lower loading, but formation of $CeVO_4$ when vanadia loading exceeded to 10% V_2O_5 . Vanadia exhibits tetrahedral properties at lower loading, but it forms Ce-O-V species onto the support surface; this exhibited the existence of highly dispersed tetrahedral species at lower loading but agglomeration at the higher extremes. Benzaldehyde production predominates with Ce-O-Ce but acetophenone is the major product with V-O-V structure.

Li et al. [120] described the oxidation process of ethylbenzene with fluorinated metalloporphyrins under a normal environment without any additives. They synthesized three different types of [5,10,15,20-tetrakis(pentafluorophenyl)] porphyrin with Fe, Mn, and Co at the centers, and Co(II)(5,10,15,20-tetrakis(pentafluorophenyl))porphyrin was found to be the ideal metalloporphyrins; these exhibited 38.6% conversion for ethylbenzene 94% selectivity towards acetophenone along with 2719 turnover numbers under optimal conditions (at 100°C and 24 h). Ma et al. [121] investigated the selective oxidation of ethyl substituted benzene with iron-containing hemin (a biomimetic system of catalysts) with molecular oxygen in acetonitrile. They reported 90.32% conversion of ethylbenzene and 94.30% selectivity toward acetophenone at 100°C under 0.3 MPa O_2 for 9 h. In situ formed 1-phenylethyl hydroperoxide (PEHP) can easily be decomposed via a hemolytic cleavage by Hemin complex to acetophenone.

Raju et al. [122] studied the aerobic oxidation of ethylbenzene without any solvent or any other additives using nickel on various supports such as SiO_2 , hydroxyapatite, SBA-15, and USY zeolites prepared by impregnation. Hydroxyapatite- and USY- (13% Na₂O) supported nickel catalysts showed better conversion and selectivity toward acetophenone due to the presence of a proper amount of comparatively weak acid sites which accelerate the formation of a major product [123], whereas the strong acid sites fasten the formation of side products [124]. Accordingly, the sample having a greater number of intermediate strength acidic points presented high conversion with reasonable selectivity to acetophenone in comparison to samples having a greater number of strong acidic points. It is also identified that additional acidic catalysts usually favor the breaking of hydrocarbons, thereby expediting the formation of more undesirable

by-products and coke that lead to the deactivation of catalysts.

In 2008, Murwani et al. [125] synthesized pure and doped high surface aluminum fluorides (HS- AlF_3) with various reactive metals like iron (Fe), vanadium (V), manganese (Mn), and niobium (Nb) by means of sol-gel fluorination. Of the four different types of reactive metals, V and Fe-doped aluminum fluoride produced the best results in ethylbenzene conversion and selectivity towards acetophenone at 60°C and solvent to TBHP ratio 1:3 since these two metals are rich with surface Lewis acid sites having abundant chemisorption capability to oxygen. It was also found that acetonitrile is the standard solvent. Mn-doped sample contained little quantity of medium-weak Lewis acid sites; however, Nb-doped aluminum fluoride exhibited very high concentration of Bronsted acid sites, on the educts that could not be necessarily activated. The functions of acid sites include (a) the activation of the tert-butyl hydroperoxide on doped metal fluorides acting as Lewis acid and redox center and (b) the yielding of acetophenone from ethylbenzene as a major product. Unfortunately, vanadium ion containing HS- AlF_3 which has a leaching effect did not show ethylbenzene conversion under reaction condition.

Salavati-Niasari [126] encapsulated copper(II) complexed with twelve-membered cyclic ligands containing three contributing atoms (N_2O_2 , N_2S_2 , and N_4) in macrocyclic ring in zeolite-Y nanocavity with a flexible ligand method in a two-step liquid phase reaction. This, first, adsorbs the ligand source, 1,2-di(o-aminophenyl-, amino, oxo, thio)ethane, N_2X_2 in the supercages of the Cu(II)-NaY and, finally, condenses the Cu(II) precursor complex $[Cu(N_2X_2)]^{2+}$ with glyoxal or biacetyl. Good catalytic action (58.2%) with high selectivity was found in ethylbenzene oxidation by zeolite encapsulated ligand complexes at 60°C using TBHP oxidant; this is because the encapsulated complexes ensure uniform dispersion of metal complexes inside the nanoporous support which gives the structural integrity. The zeolite structure can retain the visitor multiplexes dispersed and inhibit their dimerization.

In 2010, Ghiaci et al. [127] synthesized the palladium nanotubes as well as nanoparticles onto bentonite (an absorbent) modified with 3,3-(dodecylazanediy)l-bis-(N-(2-(2-aminoethylamino)-ethyl)propanamide) (DAEP) having an aliphatic tail (C-12) and a hydrophilic head. This modified bentonite, called DAEP-bentonite, was operated as a nanoreactor for the synthesis of Pd^{2+} and Pd^0 nanoparticles. They carried out oxidation of ethylbenzene and found that Pd^{2+} on functionalized bentonite along with cetylpyridinium bromide and DAEP showed higher activity compared to $Pd(0)$ onto identical support materials under similar reaction condition.

George and Sugunan [128] synthesized five different types of spinels, namely, CCr, CNCr-1, CNCr-2, CNCr-3, and NCr depending on Cu, Ni, and Cr by a coprecipitation method with the use of three consecutive nitrates such as copper nitrate, nickel nitrate, and chromium nitrate. In the liquid-phase oxidation of ethylbenzene, CNCr-2 resulted in the maximum conversion (56.1%) and selectivity (68.7%) under the same reaction condition. They also tested the

TABLE 6: Activity of graphitic nitrogen materials in selective oxidation of ethylbenzene [152].

Entry	Sample	Acetophenone (%)	Nitrogen element (%)	Oxygen element (%)	Graphitic nitrogen (%)
1	Ac-250	55.9	0.59	11	0.21
2	Ac-450	84.1	4.8	7.9	1.2
3	Ac-650	87.9	3.8	4.0	1.4
4	Ac-850	81.6	6.1	3.0	3.4
5*	Ac-850	49.9	6.1	3.0	3.4
6	Am-250	55.8	2.0	9.5	0.18
7	Am-450	86.5	2.6	7.9	0.35
8	Am-650	93.2	4.6	3.9	0.77
9	Am-850	57.9	5.2	4.6	1.1
10*	Am-850	81.9	5.2	4.6	1.1

Reaction conditions: 1 mmol ethylbenzene, 3 mmol TBHP, 10 mg catalyst, and 3 mL H₂O were put into a 50 mL sealed pressure glass vessel with magnetic stirring (80°C (*65°C)) 24 h.

efficiency of various solvents on catalytic activity and found better product in the absence of a solvent. A mechanistic scheme revealed chromite would be a convenient and eco-friendly alternative for hazardous oxidants. NHPI can efficiently improve the aerobic oxidation of hydrocarbon by combining with various mediators such as metal compounds [129–132], hemin [121], oximes [133], anthraquinones [134], *o*-phenanthroline [135], azobisisobutyronitrile (AIBN) [136], Ce(IV) [137], alkaline-earth chlorides [138], I₂/HNO₃ [139], NO₂ [140], and quaternary ammonium salts [141].

Qin et al. [142] investigated the conciliation effect of vanadium complexes on ethylbenzene oxidation using *N*-hydroxyphthalimide (NHPI) at 90°C in benzonitrile. Of the vanadium mediators used, a sequence of oxobis (8-quinolinolato) vanadium(IV) complexes synthesized by coordination of 8-hydroxyquinoline or its derivatives with oxobis (2,4-pentanedionate) vanadium(IV)(V^{IV}O(acac)₂) exhibited a better mediation effect compared to V^{IV}O(acac)₂·NH₄VO₃ and V₂O₅ giving 60–69% conversion of ethylbenzene and 97% selectivity towards ketone product under optimum reaction condition because of the dual effect of vanadium mediators on NHPI transformation to phthalimide-*N*-oxyl (PINO) radical as well as the breakdown of 1-phenylethyl hydroperoxide to acetophenone [142].

A new immobilized bidentate Schiff base oxovanadium(IV) complex was prepared [143] using chloromethylated crosslinked polystyrene microspheres (CMCPS microspheres), a starting carrier. First, the chloromethyl group of CMCPS microspheres was transferred to the aminomethyl group through Delépine reaction with a hexamethylenetetramine (HMTA) reagent forming aminomethylated (AM) microspheres (AMCPS). Secondly, the Schiff base reaction between the primary amino group of AMCPS and salicylaldehyde (SA) resulted in Schiff base-type resin microspheres (SAAM-CPS) on which bidentate Schiff base ligand SAAM were chemically attached. The subsequent coordination between the ligand SAAM of SAAM-CPS micropores and vanadyl sulfate (VOSO₄) formed heterogeneous oxovanadium(IV) complex catalyst, chemically immobilized bidentate Schiff base-type oxovanadium(IV) complex, and CPS-

VO(SAAM)₂ microspheres. This complex efficiently carried out oxidation of ethylbenzene under mild conditions with excellent reusability.

Luo et al. [144] prepared an iron nanowire-filled carbon nanotube (Fe@CNT), a magnetic separable heterogeneous catalyst by chemical vapor deposition. Selective oxidation of ethylbenzene showed that iron nanowire competently improved CNTs activity by accelerating electron transfer in dioxygen. Besides, Fe@CNTs could be recycled after consecutive six cycles with no loss of its catalytic activity simply by applying external magnetic force. Miao et al. [145] synthesized a sequence of mesoporous Cu-ZrPO (M-Cu-ZrPO) catalysts for liquid-phase ethylbenzene oxidation with a surface area of ~200 m²/g, uniform pore size of ~7.8 nm, and various copper content (0–30%) by facile one-pot evaporation. They stated that M-Cu-ZrPO can retain its thermal stability, reusability (more than five cycles), and ordered mesostructure even after heating at 700°C. Due to its stability, the activity of M-Cu-ZrPO steadily increased with raising copper contents up to 30% with conversion 91.2% and selectivity 87% towards acetophenone.

Tang et al. [152] synthesized and looked into the effect of several *N*-doped graphene in ethylbenzene oxidation. In all these reactions yielded acetophenone as the major products and little amount of benzaldehyde and benzoic acid as by-products. In the *N*-doped graphene catalytic system, it is not only the nitrogen but also the graphitic nitrogen catalyzes the conversion of ethylbenzene to acetophenone because the graphitic nitrogen is liable for TBHP activation [153]. However, too much *N*-doped graphene demonstrated an adverse effect on the activity. Usually, at high temperature, *N*-doped graphene exhibited good catalytic activity in comparison to those reacted at low temperature. Tang et al. also correlated the total nitrogen content and *N*-doped graphite in yielding of acetophenone (Table 6).

Very recently, Yao et al. [151] reported the synthesis of three novel catalysts (CuPp, MnPp, and ZnPp) by solvothermal methods and measured their catalytic activity in terms of alkylbenzene conversion. The catalysts exhibited better activities for ethylbenzene oxidation and selectivity towards acetophenone. These catalysts can be recycled by simple

filtration with no loss of catalytic ability and selectivity. Among these three catalysts, MnPp showed the highest catalytic ability and the selectivity (99%). Although the conversion rates of CoPp and CuPp catalysts were slightly lower, the selectivity exceeded more than 98%. On the other hand, ZnPp exhibited low catalytic ability in ethylbenzene conversion (40%).

4. Current Approach for Oxidation Reaction

Recently, scientists are paying more attention to use the catalysts especially heterogeneous for oxidation reactions some of them have been summarized in Table 2.

5. Future Prospects

Several heterogeneous metal complexes are available for the oxidation of alkylbenzenes at high temperatures ($>300^{\circ}\text{C}$), but the majority of the systems are not suitable for industrial conversions since the reactive intermediates are converted to various by-products that incur additional purification cost. Besides, the product distribution further depends on several factors. The profit-making interest in industrial catalysis of ethylbenzene to carbonyl compounds is a priori and must receive due interest in recent catalytic chemistry. The key barrier is the harsh reaction condition, and hence, designing a catalytic system with low cost and readily available selectivity has been challenging. The innovation of a novel method and modification of the existing techniques having clear advantages will continue to receive attention in catalyst research.

6. Conclusions

The continuous importance of aerobic oxidation of the alkyl substituted benzene to its corresponding ketone has inspired researchers to develop an efficient, green, and novel catalyst. Homogeneous catalysts have been investigated for high selectivity and conversion rate for the ethylbenzene oxidation. However, the reusable features of the supported metal catalysts have got wider acceptability even though the catalytic ability of the heterogeneous catalysts is still lower than the homogeneous ones. Lots of improvements have been made in the development of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-}$ and $\text{SiO}_2\text{-based}$ catalytic system along with various metals and organic/semiorganic linkers, and the selectivity of these systems has been demonstrated with various activators as building units. The Au/SiO_2 systems have made numerous progresses in the aerobic oxidation of alkylbenzene. Apart from this, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-based}$ catalysts have presented much reactivity and selectivity in a variety of oxidation processes. Because of the substantial improvements in product yield and catalyst reusability, heterogeneous catalysts have gained growing consideration in the recent years. The wider availability along with various physical features and porosities of several supports (e.g., mesoporous carbon hydroxyapatite, mesoporous silica, and microporous zeolite) attracts think-tank to design and generate catalytic systems as well as to explore their oxidation scheme. Porous supports along with channels and well-defined cages offer a nanoreactor environment, which can

present shape selectivity for substrates, products, and transition states.

Conflicts of Interest

The authors confirm that this article content has no conflicts of interest regarding the publication of the journal.

Authors' Contributions

This work was carried out in collaboration with all authors. All the authors read and approved the final manuscript.

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