Recent Development of Catalytic Materials for Ethylbenzene Oxidation

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Received 13 November 2019; Accepted 26 December 2019; Published 25 February 2020

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 (chalones) [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...
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 (O₂) as oxygen source [21]. Hydrogen peroxide (H₂O₂) 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 surface 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 exit 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 SiO₂/Al₂O₃ Support. Recently, the nanohybrid SiO₂/Al₂O₃ 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 SiO₂-Al₂O₃ mixed oxide supports and functionalized it with 3-aminopropyl-triethoxysilane (3-APTES) and 2-aminoethyl-3-aminopropyltrimethoxysilane (2-AE-3-APTMS) linkers (Figure 2). Thus, functionalized oxide was further functionalized with Schiff base by conjugating it to Mn(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 SiO₂-Al₂O₃ mixed oxide supports combining two diverse linkers, 3-APTES and 2-AE-3-APMTMS (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 SiO₂-Al₂O₃ mixed oxide supports using 2-AE-3-APMTMS (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 SiO₂-Al₂O₃ 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 bipyrindylketone over the nanohybrid SiO₂/Al₂O₃ 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 SiO₂-Al₂O₃ support (Figure 3) [48]. This performed ethylbenzene oxidation in N-hydroxyphthalimide (2-hydroxy-1H-isooindole-1,3-dione (NHPI)) with 82% selectivity in an oxygen atmosphere and acetic acid solvent at 100°C. Very recently, SiO₂-Al₂O₃-APTS-MBPK-IVII and SiO₂-Al₂O₃-APMTMS-MBPK-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 SiO₂-Al₂O₃ (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 (SiO₂) 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 physio-chemical properties; these provide well dispersion of metal
Table 1: Homogeneous catalysts in ethylbenzene oxidation.

| Catalysts | Oxidant | Reaction conditions | 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$_2$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-diazeniabicyclo [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-methylimidazoliumbromide | 100 | 7 | Acetophenone | — | 77 | [43] |
| 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$^+$ oxidation                     | [56] |
|      | MnO$_2$ hollow sphere                         | Precipitation                 | Formaldehyde oxidation               | [57] |
|      | Ruthenium catalyst                           |                               | Water oxidation                      | [58] |
|      | Solid catalyst on various supports           | Impregnation                  | 1-Octanol oxidation                  | [59] |
| 2018 | 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] |
|      | Porphyrinic metal-organic framework          | Postsynthetic modification    | Cyclohexane                          | [65] |
|      | MnO$_2$-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] |
|      | Boron-doped crystalline diamond              |                               | Aliphatic polyamine oxidation        | [69] |
| 2015 | Pd/graphene                                   | Sonoelectrochemical and chemical-reduction | Glucose oxidation                   | [70] |
|      | PdO/graphene                                  | Cyclic voltammetry (CV) and chronoamperometry (CA) | Ethanol oxidation                   | [71] |
|      | Graphene-supported palladium                 |                               | Formaldehyde oxidation               | [72] |
|      | PtAg bimetallic alloy                         | Coreduction                   | Methanol oxidation                   | [73] |
|      | Pt/carbon aerogel 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] |
| 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 | Coreduction | Ethanol oxidation | [79] |
|      | Pd nanohollow/Pt nanorod core/shell composite | Multistep crystalline growth | Methanol oxidation | [80] |
| 2013 | 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] |
|      | Au/CuO | Coprecipitation | Carbon monoxide | [84] |
| 2012 | 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 | Ethanol oxidation | [87] |
|      | Au-Pd/MgO | Sol immobilization, adsorption-reduction | Benzyl alcohol oxidation | [88] |
| 2011 | Pd-Ni electrocatalysts | Nanocapsule | Ethanol oxidation | [89] |
| 2010 | PtBi/C electrocatalysts | Borohydride reduction | Ethanol electrooxidation | [90] |
|      | PdIr/C | Simultaneous reduction | Ethanol oxidation | [91] |
|      | PtSn/C-Rh, PtSn/C-CeO | Alcohol reduction, polymeric precursor | Ethanol oxidation | [92] |
| 2009 | Gold nanoparticles | Reduction | Glucose and 1-phenyl ethanol | [93] |
|      | Supported gold nanoparticles | — | Silanol oxidation | [94] |
| 2008 | Metalloporphyrin and cobalt acetate | Condensation | p-Xylene oxidation | [95] |
|      | 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] |
| Name of catalysts | Substrate      | Oxidant | Reaction time (h) | Reaction temperature (°C)/solvent | Conversion (%) | Selectivity (%) | Ref. |
|------------------|----------------|---------|-------------------|-----------------------------------|---------------|-----------------|------|
| SiO₂/Al₂O₃-APTMS-BPK-Mn, NHPI | Ethylbenzene  | O₂      | 8                 | 100/acetic acid                   | 53            | 74              | [45] |
| SiO₂/Al₂O₃-APTMS-BPK-Co(II), NHPI | Ethylbenzene  | O₂      | 8                 | 100/acetic acid                   | 81            | 98              | [45] |
| Nanohybrid SiO₂/Al₂O₃ supported cobalt, NHPI | Ethylbenzene  | O₂      | 8                 | 100/acetic acid                   | 64            | 82              | [48] |
| Nanohybrid SiO₂/Al₂O₃ modified Fe nanocatalysts | Ethylbenzene  | TBHP    | 24                | 50/solvent free                   | 40            | 89              | [47] |
| Nanohybrid SiO₂/Al₂O₃ supported cobalt | Ethylbenzene  | TBHP    | 24                | 100/solvent free                  | 47            | 79              | [49] |
| Mn nanocatalysts modified on nanohybrid SiO₂/Al₂O₃ | Ethylbenzene  | TBHP    | 24                | 100/solvent free                  | 67            | 84              | [28] |
| SiO₂-Al₂O₃ mixed oxide immobilized Mn catalysts | Ethylbenzene  | TBHP    | 24                | 80/solvent free                   | 67            | 93              | [44] |
| SiO₂-Al₂O₃ mixed oxide immobilized cobalt catalysts | Ethylbenzene  | TBHP    | 24                | 80/solvent free                   | 86            | 99              | [29] |
| Mn supported on SiO₂-Al₂O₃, scCO₂ | Ethylbenzene  | TBHP    | 24                | 120/CO₂                          | 86            | 88              | [46] |

NHPI = N-hydroxyphthalimide; BPK = bipyridylketone; APTMS = trimethoxysilylpropylamine; SC = supercritical.
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 H₂O₂, 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 corresponding 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 [Mn(TMCP)]/[TMCP: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...
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 alkyl-benzene 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 NHPI 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 constant 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 Co(CH3COO)2·4H2O [106]. The catalysts exhibited 98% conversion and 99% selectivity towards ketone products in the presence of NHPI under an O2 atmosphere. Neeli et al. [24] prepared Cu/SBA-15 catalysts by loading Cu via impregnation wherein Cu(NO3)2·3H2O 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 Fe3O4 solid matrixes. The catalysts become active upon the removal of the hard template of the silica supports.
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$_2$O$_2$ 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.
(60%). The presence of a pyridine group to the axial site of Co(III) cyclam composite was further investigated, confirming 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-N02TDCPP)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 catalytic effect of MnO4−-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−-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 tetraaza 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 CO3− 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 CO3− 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     | H₂O₂               | 24        | 80/tert-butanol, acetone, water | —                                     | —              | —               | [25] |
| Silica gel supported cobalt, NHPI                     | O₂                 | 24        | 100/acetic acid   | 98                                    | 99             | [106]           |
| Cu/SBA-15                                             | TBHP               | 5         | 90/solvent free   | 94                                    | 99             | [24]            |
| Metalloporphyrin@SiO₂                                  | Ethylbenzene       | O₂        | —                 | 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                         | O₂                 | <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 SiO₂@Fe₃O₄ core/shell | O₂                 | 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            |                    | 5.5       | Room temperature/acetonitrile | 66                                    | 66             | [110]           |
| Zeolite-encapsulated Cu (II)                           | H₂O₂               | 8         | 70/benzene        | 46                                    | 66             | [115]           |
| MnO 4-1 exchanged Mg-Al hydrotalcite                    | O₂                 | 5         | -/solvent free    | 22                                    | 98             | [116]           |
| Cu(tacn)(ClO₄)₂                                         | TBHP               | 10        | 60/acetonitrile   | 49                                    | 91             | [117]           |
| Ni/Al hydrotalcites, CO₃⁻                               | O₂                 | 5         | 135/solvent free  | 47                                    | 99             | [118]           |
| Vanadia/ceria                                          | H₂O₂               | 6         | 60/acetonitrile   | 20                                    | 72             | [119]           |
| Cobalt(II)(5,10,15,20-tetrakis(pentafluorophenyl))porphyrin | O₂                 | 24        | 100/solvent free  | 38                                    | 94             | [120]           |
| Hemin/NHPI                                             | O₂                 | 9         | 100/acetonitrile  | 92                                    | 94             | [121]           |
| Supported nickel                                        | O₂                 | 5         | 150/solvent free  | 20                                    | 80             | [122]           |
| Metal-doped HS-ALF₁                                    | TBHP               | 6         | 60/acetonitrile   | 70                                    | 72             | [125]           |
| Macro cyclic copper (II) complex                        | TBHP               | 10        | 60/acetonitrile   | 62                                    | 88             | [126]           |
| DAEP-bentonite-Pd (II)                                 | TBHP               | 24        | 80/solvent free   | 92                                    | 93             | [127]           |
| Ni substituted copper chromite spinel                   | THBP               | 8         | 70/acetonitrile   | 56                                    | 68             | [128]           |
| Vanadium complex/NHPI system                           | O₂                 | 12        | 90/Benzonitrile   | 69                                    | 97             | [142]           |
| Mesoporous Cu-ZrPO                                     | THBP               | 24        | 80/Benzonitrile   | 91                                    | 87             | [145]           |
| Immobilized bidentate Schiff base oxovanadium(IV) complex | O₂                 | 14        | 110/solvent free  | ~40                                    | 98             | [143]           |
| Fe@CNT                                                 | O₂                 | 3         | 155/acetonitrile  | 36                                    | 60             | [144]           |
| Supported Co₅H₂P₂Mo₁₅V₃O₆₂                              | H₂O₂               | —         | 70/glacial acetic acid | 72                                    | 95             | [146]           |
| µ-Oxo dimeric metalloporphyrins                         | O₂                 | 2         | 65/solvent free   | 91                                    | 99             | [147]           |
| Cobalt-supported catalysts on modified MNPs            | O₂                 | 10        | 100/ethanol       | 88                                    | 98             | [148]           |
| Carbon nanotube                                         | O₂                 | 4         | 155/acetonitrile  | 40                                    | 62             | [149]           |
| Mn/N-C/Al₂O₃                                           | O₂                 | 6         | 120/solvent free  | 27                                    | 99             | [150]           |
| Mesosubstituted pyrazolyl porphyrin complexes          | TBHP               |           | 80/water          | 99                                    | 99             | [151]           |

Tacn = triazacyclononanone; 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/beryllium 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 CeVO4 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 molecular oxygen in acetonitrile. They reported 90.32% conversion of ethylbenzene and 94.30% selectivity toward acetophenone at 100°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 eucts 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-AlF3 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 (\( N_2O_2 \), \( N_2O_3 \), and \( N_2 \)) 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, Ghiauci et al. [127] synthesized the palladium nanotubes as well as nanoparticles onto bentonite (an absorbent) modified with 3,3-(dodecylazanediyil)-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.

The 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], azobisisbutyronitrile (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-pentanedionato) vanadium(IV) VO(acac)2 exhibited a better mediation effect compared to VO(Oacac)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 groups through Delépine reaction with a hexamethylenetetramine (HMTA) reagent forming aminomethylated (AM) microspheres (AMCPS). Second, 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 micro pores and vanadyl sulfate (VOSO4) formed heterogeneous oxovanadium(IV) complex catalyst, chemically immobilized bidentate Schiff base-type oxovanadium(IV) complex, and CPM-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 CuPp and ZnPp 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°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 SiO2-Al2O3- and SiO2-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/SiO2 systems have made numerous progresses in the aerobic oxidation of alkylbenzene. Apart from this, SiO2-Al2O3-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 hydroxypatite, 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.

Acknowledgments

This research was funded by the Deanship of Scientific Research at Princess Nourah bint Abdulrahman University through the Fast-track Research Funding Program.

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