REVIEW

Catalytic Organic Reactions in Liquid Phase by Perovskite Oxides: A Review

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The structural flexibility and controllable physico-chemical characters of perovskite oxides have drawn major attention of researchers for catalytic reactions. Perovskite oxide are mainly used as catalysts for electrochemical, high temperature gas-phase and photocatalytic reactions but their uses for catalytic organic reactions in liquid phase are limited. Various porous and nano-perovskite oxides have been prepared by different methods are effectively used as catalyst for different types of organic reactions in liquid phase. The liquid-phase catalytic organic reactions over perovskite oxides have been classified mainly into three groups: (i) acid/base catalyzed, (ii) selective oxidation and (iii) cross-coupling reactions. This review article mainly emphases on different examples of perovskite oxides catalyzed organic reactions in liquid phase along with the relationships among the unique catalytic performance with the structural and the physico-chemical properties of perovskites.

Keywords: Organic reactions, Liquid-phase, catalyst, Perovskite oxides, Structures.

INTRODUCTION

Modern day's chemical industry is in need of technology for generation of sustainable as well as environmentally-safe chemical processes [1-12]. In state of conventional technologies, catalytic processes can apply for the production of various industrially important chemicals due to its economic and environmental benefits. Numerous homogeneous catalysts have been industrially applied for catalytic organic reactions in liquid phase through green synthetic route. These catalysts are highly active as well as selective due to their structure and precisely controllable reactivity [13]. However, the major disadvantages of homogeneous catalysts for large scale application in industrial processes are catalyst separation and various problems in reuse of these costly catalysts [14-16]. These disadvantages can be circumvented through the use of easily recyclable heterogeneous catalysts for the environmental friendly synthesis of expensive important chemicals. Several metal hydroxides or oxides [17-20], polyoxometalates [21,22], zeolites [23,24], metal nanoparticles [25,26], metal-organic frameworks [27,28], polymers [29,30], dendrimers [31] and carbon-based materials [32,33] have been efficiently applied as heterogeneous catalysts for organic reactions in liquid-phase.

Recently, perovskite oxides (with common formula ABO_3) have drawn much attention due to their versatile applications likes magnetic, multi-ferroelectric, piezoelectric, superconducting and also heterogeneous catalytic properties [34-51]. Different perovskite oxides were studied as catalyst for electrochemical reactions [34-38], high temperature gas-phase reactions [39-49] and photocatalytic [47-51] due to their structural stability, flexibility, diversity and controllable physico-chemical properties. Though industrially important perovskite catalyzed organic reactions in liquid-phase have been limited reports [52-88]. Recently several researchers reported porous nano perovskite oxide synthesized by different methods could be used as heterogeneous catalyst for organic reactions in liquid-phase such as acid/base-catalyzed organic reactions [52-57], selective oxidations [58-76], cross-coupling reactions [77-81] and some other hydrogenation/oxidation reactions [82-88]. Table-1 listed various examples of perovskite oxide-based materials as heterogeneous catalyst for organic reactions in liquid phase.

Numerous examples of perovskite oxide catalyzed organic reactions in liquid-phase are highlighted in this review. In addition, their synthesis, structures, physico-chemical properties and environmental-friendly catalytic applications are also summarized.

TABLE-1
VARIOUS HETEROGENEOUS PEROVSKITE OXIDE CATALYSTS FOR ORGANIC REACTIONS IN LIQUID PHASE

Catalyst/additive	Reaction	Yield	Time (h)	Ref.
Acid/base-catalyzed reaction				
$BaZrO_3$		53	1.5	[52]
$HTiNbO_5$ nanosheets		17	6	[53]
$SmFeO_3$		98	1	[54]
Mesoporous $ZnTiO_3$		90-94	14-24	[55]
Mesoporous $ZnTiO_3$		73-92	15-18	[55]
$ZnTiO_3$/CTAB		71-94	8	[56]
$BiFeO_3$		63-88	–	[57]
Selective oxidation				
Cu/$LaFeO_3$		99	3	[58]
$LaCrO_3$		84-97	7-8.5	[60]
$KNbO_3$		30, 70	1	[61]
$Y_2BaCuO_{5\pm x}$		18, 14, <1	0.5	[62,63]
$CuZrO_3$		69	2	[64]
AuPd/$LaMnO_3$ NaOH		70, 17	6	[65]

Catalyst	Reaction	Yield (%)	Time	Ref.
$Pd_{0.002}K_{0.17}Ti_{1.86}Sr_{0.20}O_4$ $Pd_{0.03}K_{0.03}Ti_{1.47}Sr_{1.02}O_4$	Oxidation of secondary benzylic alcohol, O_2, 120°C, toluene	30-99	24	[66]
La_2CuO_4	Benzaldehyde to benzoic acid, Air, 75-80°C, EtOAc	70-90	–	[67]
$SrMnO_3$	Oxidation of secondary benzylic alcohol, O_2, 50-80°C, toluene	81-99	1-10	[68]
$SrMnO_3$	Ar-CH$_2$-Ar to Ar-CO-Ar, O_2, 60-120°C, n-octane	81-94	8-24	[70]
$BaFeO_{3-\delta}$	C–H oxidation, O_2, 80-90°C, PhCF$_3$	14-59	72-96	[71]
$BaRuO_3$	Sulfide to sulfoxide + sulfone, O_2, 40-100°C, t-BuOH	50-90	12-60	[72]
$(La,Sr)_{0.5}(Co,Mn)_{0.5}O_{3-\delta}$/ NHPI	p-xylene to terephthalic acid, O_2, 90°C, AcOH	99	99	[73]
$KTaO_3$	Styrene to benzaldehyde, Acetonitrile, 60°C, H_2O_2	58	4	[74]
$BaFeO_{3-\delta}$	Alkene cleavage, O_2 (1 MPa), PhCF$_3$, 363K $R_1,R_2,R_3=$ Ar,R,H,etc	75	30	[76]

Coupling Reaction

Catalyst	Reaction	Yield (%)	Time	Ref.
$LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$/base-TBABr	Ar–X + Ar–B(OH)$_2$, 80°C, IPA/H$_2$O	26-95	0.5-18	[77,78]
$La_{0.9}Ce_{0.1}Co_{0.6}Cu_{0.4}O_3$/base-EtOAc	Phenol + Ar–X, 110°C, Toluene	46-90	48	[79]
$La_{0.9}Ce_{0.1}Co_{0.6}Cu_{0.4}O_3$/base	Ar–X + terminal alkyne, 120°C, H$_2$O/DMA	47-96	6-24	[80]
$Bi_{1.97}Eu_{0.03}MoO_6$	2-aminobenzophenone + ethyl acetoacetate, H_2O, 35-45°C → quinoline product	90-97	0.5-1	[81]

	Other Reaction			
LaFeO₃/KOH	Nitrobenzene (R) → Aniline (R); IPA, reflux	78-98	2-6	[82]
LaCo₀.₈Fe₀.₂O₃	Cinnamyl alcohol → Cinnamaldehyde; TBHP, 50°C, CH₃CN	89	6	[84]
Pt/YCo₀.₃Fe₀.₇O₃	Benzylideneacetone → alcohol; TBHP, 90°C, 2 MPa H₂, isopropanol/water	95	0.5	[85]
LaMnO₃	Xanthene → Xanthone; O₂, Heptane, 353K	99	24	[86]
LaMnO₃	2-Naphthol → BINOL; O₂, Heptane, 333K	66	24	[86]
LaMo₀.₁Fe₀.₉O₃	Naphthol + barbituric acid derivative (X=O,S; Y=H,Me) + aldehyde (R) → fused product; CHO, Solvent free, 100°C	92	0.3	[87]
LaMnO₃	Furfural → Furfuryl alcohol; Isoproponol, N₂, 180°C	95	3	[88]

Synthesis and structure of perovskite catalysts: A number of combination of A- and B-site is possible to procedure ABO₃ structure of perovskite oxide [46,89,90]. Partial substitution of either or both sites (A and B) by other metals can control metal cation's oxidation states and oxygen stoichiometry in multi-component perovskite compositions. Therefore, the adjustable composition of perovskites could lead to structure flexibility with useful physico-chemical characters. Many wonderful books and articles presented the synthesis, structures, characteristic features and uses of perovskite oxides in detail [34-51].

Synthesis of perovskite catalysts: The purity, surface area, particles size or shape and pores size/amounts of perovskite oxides are strongly depending on their synthesis methods [34,89,90]. Ultrapure perovskites can be prepared from pure metal component by the solid-state synthesis method but these synthesized perovskites are mainly use for electrical and electronic applications. But the enormously low surface area (~ 1 m² g⁻¹) of these perovskite limits their overall performance as effective bulk catalyst [4]. Liquid-phase organic reactions are mainly performed under mild reaction conditions; therefore, relatively high surface area of perovskite catalysts is one of most important factor for a highly efficient catalytic system. Generally, perovskite oxide catalysts are prepared by co-precipitation [65,67-69], solgel [61,64,65,69-73], solution combustion [57,58] and hard-soft templating [82] methods. In co-precipitation, a suitable precipitant (NaOH, ammonia, amines) is slowly mixed to an aqueous two or more metal salts solution generally as metal nitrate and gives a homogeneous mixture. The resultant precipitates wash with pure solvents then calcine at a proper temperature. Different perovskites, ABO₃ (A = La, Sm, Pr and B = Fe, Cr, Mn, Ni, Co), are synthesized by co-precipitation method using *n*-butyl amine as a precipitant [68]. A super-critical anti-solvent precipitation method is also used for the synthesis of LaBO₃ (B = Fe, Cr, Co, Ni, Mn) with high surface areas (22-52 m² g⁻¹) [65]. In co-precipitation method, soluble metal complexes are produced in precipitation step and particular cations are also loss in washing step. Thus controlling the composition of perovskites is difficult in this method.

Perovskites with controlled chemical composition as well as relatively high surface areas are prepared by simple and useful sol-gel method. Malic acid and citric acid most frequently used in sol-gel method for synthesis of perovskites [91,92]. $La_{0.8}Sr_{0.2}MO_3$ (M = Co and Mn with surface area 20 $m^2 g^{-1}$ and 37 $m^2 g^{-1}$, respectively) with high surface-area have synthesized from aqueous metal salts solution and malic acid at pH 3-4 [92]. The polymerized complex method and the Pechini method have also been well-studied for perovskites synthesis [93,94]. Hexagonal $SrMnO_3$ (surface area 25 $m^2 g^{-1}$) have synthesized by polymerized complex method [69]. $SrMnO_3$ with appreciable large surface area ($\leq 47 m^2 g^{-1}$) also fruitfully synthesized without pH adjustment by using metal acetates and aspartic acid rather than metal nitrates [70] and other hexagonal perovskite materials was also synthesized by this method [71,72].

The single step solution combustion method is also use for synthesis of perovskite nanoparticles, which involves the combustion of corresponding metal salts (mostly nitrates and chlorides in some cases) with appropriate organic fuels (citric acid, urea, glycine, glycerol, *etc.*). The reaction itself supplied the required heat for phase formation. Therefore, heating temperature is lower than the conventional paths and calcination step is not required. The copper substituted $LaMO_3$ (M = Fe, Mn, Co) catalysts with surface area 10-27 $m^2 g^{-1}$ was synthesis by single-step solution combustion method [58]. This synthesis method has also been useful for rapid synthesis of different multicomponent perovskites. But, it is difficult to control parameters of the process and maintains the quality of final product by using this preparation method.

Soft and hard templating methods most comprehensively studied for the preparation of porous perovskite materials by using porous silicates and polymeric materials [48]. The perovskite nanoparticles have no pores and the reaction happens only on the surface of the catalyst, which restrict the overall catalytic performance [68]. The $ZnTiO_3$, mesoporous perovskite, with 136 $m^2 g^{-1}$ surface area and 5.1 nm averaged pore dimension was synthesized by using a nonionic surfactant template (Pluronic P123) in a new evaporation-induced self-assembly method [61]. Hence, the soft and hard templating methods provide large surface areas (> 100 $m^2 g^{-1}$) with orderly pore structures but the method complicity, requirement of costly templates and also difficulty in their successive removal makes the applicability of this method is limited.

Although, nanosized and porous suitable perovskite oxides prepared by the aforesaid methods are mainly applied as efficient catalysts. The typically inactive perovskite oxides may be used as supports for different supported metal catalysts and a synergistic effect of perovskite oxide and metal nanoparticles has been suggested for some reactions [65,73,85]. The details applications of all these perovskite oxides for catalytic organic reactions in liquid-phase are described as follows:

Structure of perovskite catalysts: The perovskite oxides are ideally cubic in crystal structure, where large cations (A) have twelve-fold and smaller cations (B) have six-fold coordination with BO_6 octahedra corner-sharing [4]. The tolerance factor (t) is used for indexing the deviation from this ideal structure and is estimated from eqn. 1 (r_A = cationic radius of A, r_B = cationic radius of B and r_O = anionic radius of O^{2-}) [89,90].

$$t = \frac{(rA + rB)}{\sqrt{2(rB + rO)}} \qquad (1)$$

The ideal cubic perovskite has t value 1. When the t value is lower than 1 (0.75 to 1), the perovskite gives tetragonal, rhombohedral, or lower symmetric structure [89]. The greater t values (> 1) are obtained when we use large alkaline-earth metal cations (A^{2+}) or small B cations and showing hexagonal crystal structure with BO_6 octahedra face-sharing [70,71]. Two-dimensional perovskite with inter leaved cations are showing layered structures is also reported [89].

Different perovskite oxides are design for catalytic organic reactions in liquid-phase. The crystalline structure, formation of oxygen vacancy and the oxidation state of B can be changed by controlling the chemical composition of perovskite oxides. When an A^{3+} ion is replaced by an A^{2+} cation from $A^{3+} B^{3+} O_3$ then increased the oxidation state of B or formed oxygen vacancy [4]. The details applications of all these perovskite oxides as catalyst for organic reaction in liquid-phase along with the relationships between the unique catalytic properties and the structural, the physico-chemical properties are also discussed.

Catalytic applications of perovskite oxide for organic reactions in liquid-phase: The catalytic activity of perovskite oxides strongly depends on their physico-chemical properties. It has been reported that crystalline structure [69,70], formation energy for oxygen vacancy [71], oxygen adsorption capacity [65], surface oxygen vacancy [64,73] and oxidation state of B cation [72] play significant roles for the perovskite oxide catalyzed organic reactions in liquid phase. Several absorptions, spectroscopic and computational methods have been used for characterization of the redox and acidic-basic properties of perovskite oxides [21-23,25,26,29]. The oxygen mobility and reducibility are usually analyzed by hydrogen temperature programmed reduction (TPR), isotopic exchange experiments and temperature programmed desorption (TPD) for the characterization of redox properties. Adsorption micro-calorimetry, site titration using Hammett indicators, TPD and spectroscopy are exclusively used for the analysis of surface acidity/basicity of perovskites. The bulk and surface structures are characterized by infrared spectroscopy (IR), X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and high resolution transmission electron microscope (HRTEM) measurements. However, most publications mainly focus on development of perovskite oxide-catalyzed organic reactions in liquid-phase. Hence, such characterizations in most systems are incomplete and lack of comprehensive mechanistic studies. In this review, the important catalytic property of perovskite oxides in liquid phase is comprehensively summarized and some of the reaction mechanism along with the characterization results is also discussed.

Acid/base-catalyzed reactions: The petroleum refining and petrochemical industry have been utilized solid acid-bases as catalysts for lots of important processes [95-100]. Zeolites,

clays, resins, hetero polyacids, mono or mixed metal oxides and a catalyst with surface modification have been extensively examined as acid-base catalyst. However, the performance of perovskite oxides as acid-base catalyst are still under explored. In recent times, a review article systematically summarized catalytic performance of perovskites as acid-base catalyst [42]. The effects of density, strength, surface modification, exposed faces and type of acid-base sites of perovskite oxides to their performance as catalyst have been studied for the conversion of 2-propanol [53]. In contrast, acid-base catalysis in liquid-phase and comprehensive reaction mechanisms studies are still limited.

$HSr_2Nb_3O_{10}$ and $HTiNbO_5$ nanosheets with modified surface area were reported as acid catalysts for acetic acid esterification, cumene cracking and 2-propanol dehydration [53]. Cyanosilylation with trimethylsilyl cyanide (TMSCN) of carbonyl compounds to corresponding cyanohydrins trimethylsilyl ethers is a key reaction for production of α-hydroxy aldehydes or acids and β-amino alcohols. $SmFeO_3$ showed significant activity towards the catalytic cyanosilylation of benzaldehyde by trimethylsilyl cyanide in comparison to other catalysts used for this reaction [54]. But, it is proposed that the active sites of $SmFeO_3$ was the Brønsted acid sites but results were lack of detail characterization. A new mesoporous $ZnTiO_3$ perovskite was developed as an efficient catalyst for Friedel-Crafts alkylation by benzyl chloride along with the esterification of C_{12}-C_{18} carboxylic acids [55,56]. A probable mechanism was suggested for the $ZnTiO_3$-catalyzed esterification that carboxylic acid was activated through coordination with the Lewis acid site. The same group also stated that reusable nano $ZnTiO_3$ base catalyst with cubic structure prepared *via* sol-gel method for 1,6-naphthyridine synthesis in water [56]. The cooperative action of Ti^{4+} as Lewis acid site and O^{2-} as base site for the probable reaction mechanism is also proposed.

Preparation of hydroxypivaldehyde is a key reaction, since the product gives neopentyl glycol on successive hydrogenation and it is an intermediate of plasticizers, polyesters, lubricants and synthetic paints. $SrZrO_3$ and $BaZrO_3$ exhibited good catalytic activity towards this base-catalyzed aldol condensation reaction of isobutyl aldehyde by formaldehyde with 53% yield along with 91% conversion [52].

Different dihydro-2-oxypyrroles was synthesized by one-pot synthesis from dimethyl acetylene dicarboxylate, formaldehyde and anilines in methanol over $BiFeO_3$ catalyst at room temperature [57]. An external magnet could easily recover the used catalyst from the reaction medium and the recovered catalyst was efficiently reused. The authors proposed that an imine intermediate was activated through Lewis acid sites of $BiFeO_3$ helps a Mannich type reactions by successive cyclization reactions, even though there was no physico-chemical evidence regarding this acid sites.

Selective catalytic oxidation: Selective catalytic oxidation of petroleum-based feed stocks into suitable compounds is a significant reaction since the products are extensively applied for synthesis of valuable products and important chemicals [101-108]. The CO oxidation and total oxidation of different hydrocarbons are extensively reported over perovskite oxide catalysts [39-43,84]. Several efficient perovskite oxides catalysts are used for selective oxidation reactions in liquid phase by using molecular oxygen (O_2), hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (TBHP) as oxidant [58-76]. The kinds of catalyst and oxidant played important role for the catalytic efficiency as well as for the reaction mechanism. Preparation of particular widely used important carbonyl compounds from corresponding alcohols *via* selective oxidation due to production of fine chemicals and pharmaceuticals products. Copper-substituted $LaFeO_3$($Cu/LaFeO_3$) perovskite developed as a reusable catalyst for selective oxidation of benzyl alcohol with TBHP [58]. The combustion synthesized catalyst showed higher activity due to the presence of a peculiar poorly-defined amorphous CuO along with substitutional Cu^{2+} phase on the top of $LaFeO_3$ particle. Cerium doped rhombohedral $La_{1-x}Ce_xCoO_3$ nano perovskite was also act as an effective catalyst for the same reaction in liquid medium under atmospheric pressure using highly pure oxygen as oxidant. Under optimum reaction conditions, among the prepared catalysts $La_{0.95}Co_{0.05}O_3$ catalyst showed higher catalytic activity (> 35%) with ~ 100% selectivity upto four cycles [59]. Reusable $LaCrO_3$ catalyst also reported for the oxidation of alkyl arenes using TBHP under solvent-free condition [60]. However, H_2O_2 and O_2 have received much consideration than organic hydroperoxides due to their environmental-friendly nature (gives water only as byproduct) and also content high active oxygen species. Titanium loaded potassium niobates ($KTi_{0.2}Nb_{0.8}O_3$ and $KTi_{0.1}Nb_{0.9}O_3$) perovskite developed for the selective catalytic oxidation of 2-(methyl-thio)benzothiazole with excess H_2O_2 to the analogous sulfone and sulfoxide [61]. The electronic and structural defects were due to incorporation of titanium ions into the perovskite lattice for the higher activity of titanium substituted catalyst than the pure potassium niobates ($KNbO_3$). The $Y_2BaCuO_{5\pm x}$ perovskite was also reported as recyclable efficient catalyst for the selective catalytic oxidation of phenol to hydroquinone and catechol using H_2O_2 [62,63]. A radical substitution mechanism is proposed but the complete mechanism was still uncertain for the oxidation reactions with H_2O_2.

Catalytic oxidative promoting reactions of biomass-derived substance into valuable chemicals with O_2 are an important matter to make a sustainable society due to the replacement of non-renewable fossil resources [7-12,109]. However, still now the selective liquid-phase heterogeneous catalytic oxidation under mild conditions with O_2 are limited [101-108,110]. The CuO and $CuZrO_3$ mixture was developed as heterogeneous catalytic oxidation of vanillyl alcohol (a model compound representing lignin) [64]. The redox properties of the catalyst improved due to the presence of Cu-O-Zr linkages in high concentration as active phase. The perovskite-catalyzed aerobic oxidation of common organic substances was also examined by various researchers. The effect of perovskites supports on glycerol aerobic oxidation was exclusively studied over AuPt nanoparticles supported on lanthanum based oxides $LaMO_3$ (M = Fe, Cr, Mn, Ni, Co) [65]. This oxidation gives different products and the selectivity of the products was depending on the perovskite supports. From mechanistic studies, it was suggested that the oxygen adsorption capacity supports strongly

influence selectivity of the product and LaMnO₃ support inhibits the lactic acid production due to high oxygen capacity. The Pd-containing perovskite oxide (Pd/K$_{0.6}$Ti$_{1.85}$O$_4$) was reported as a highly stable and reusable catalyst for allylic and benzylic alcohols oxidation by using oxygen [66]. Various substituted benzaldehyde with electron-withdrawing and electron-donating groups were selectively oxidized to the desired products over La$_2$CuO$_4$ catalyst [67].

The catalytic oxidation over various types of pure rhombohedral and hexagonal perovskite oxides (BaFeO$_{3-\delta}$, BaRuO$_3$ and SrMnO$_3$) with relatively high surface areas are also reported as efficient catalyst for oxidative dehydrogenation of alcohols and other difficult aerobic oxidation of alkanes and sulfides [69-72]. These hexagonal perovskites also selectively catalyzed alcohols, alkanes, alkyl arenes and sulfides in presence of O$_2$. Many allylic, aromatic and heteroatom-incorporated primary or secondary alcohols were selectively transformed to the desired carbonyl compounds over hexagonal SrMnO$_3$ [69]. But the catalyst showed low catalytic activity towards aliphatic alcohols oxidation. The kinetics measurement showed non-dissociative alcohol and oxygen adsorption and Langmuir-Hinshelwood mechanism was proposed for this catalyzed oxidation reaction. The C-H bond breaking was suggested for the rate determination step from kinetic isotope effect. This type of O$_2$-activation was also used for oxidative homocoupling reactions of phenols and amines and the selective oxidation of alkyl arenes to corresponding oxygenated/dehydrogenated products. This is the first example of reductive O$_2$ activation for selective catalytic oxidation over SrMnO$_3$ in liquid-phase. The kinetic measurement showed that an oxygen species generated from the solid compare to SrMnO$_3$ is responsible for this oxidation process and Mars-van Krevelen mechanism was proposed for this reaction [111]. Various aromatic and aliphatic sulfides could also efficiently catalyze to the corresponding sulfones and sulfoxides by using O$_2$ over recyclable rhombohedral BaRuO$_3$ [71]. The oxygen transfer reactivity of ruthenium based oxides was significantly affected by the crystal structure of oxides. Thus, the oxygen easily transferred to a sulfide from BaRuO$_3$ and oxygen also re-oxidized the partially reduced BaRuO$_{3-x}$ than other Ru-based perovskites. The aliphatic C-H bond oxidation of alkanes produces industrially important chemicals and it is still challenging in the chemical industries [72]. There are few Ru- and V-based perovskites used as recoverable as well as a reusable heterogeneous catalyst for aerobic oxidation of adamantane [112,113]. Hexagonal, recyclable 6H-BaFeO$_{3-\delta}$ ($\delta = 0.1$) was efficiently catalyzed this oxidation as well as other various hydrocarbons in presence of oxygen [72]. The author proposed that the adamantane oxidation gates through a radical-mediated pathway and abstraction of hydrogen by BaFeO$_{3-\delta}$ suggested for the rate determining step. The oxygen-deficient, orthorhombic, recyclable (La,Sr)$_{0.5}$(Co,Mn)$_{0.5}$O$_{3-\delta}$ perovskite was basically applied for the selective oxidation of ethylbenzene and toluene to acetophenone and benzoic acid, respectively with N-hydroxyphthalimide (NHPI) [73]. It has been proposed that the large oxygen vacancies of this perovskite could activated NHPI to produce phthalimide N-oxyl radical (PINO) and the radical promoting the formation of an alkyl radical through hydrogen abstraction from hydrocarbons. However, mechanistic detail is still required.

A sets of alkaline tantalates (NaTaO$_3$, LiTaO$_3$, KTaO$_3$) also selectively catalyzed styrene to form benzaldehyde. The highest conversion (~ 58%) with 77% selectivity was achieved for KTaO$_3$ upto six catalytic cycles. It is suggested that the increasing catalytic performance was attributed to crystalline structure of perovskites, the atomic radius of the alkaline-metals and the presence of segregated phases in the component [74]. Sol-gel methods synthesized, pure and Co loaded nano-lanthanum ferrite (LaFe$_{1-x}$Co$_x$O$_3$; $x = 0$ to 1) were also examined for selective catalytic oxidation of styrene to benzaldehyde using H$_2$O$_2$ as oxidant [75]. The catalyst showed the higher activity at lowest substitution than other higher cobalt loaded ferrite and also than for pure LaFeO$_3$.

BaFeO$_{3-\delta}$ perovskite may well affectively catalyzed oxidative C=C bond cleavage of numerous aromatic alkenes to preferred carbonyl compounds (~ 75% yield) under the additive free condition with O$_2$ as oxidant [76].

Cross-coupling reactions: Several significant organic chemicals (drugs, materials, optical devices, *etc.*) are manufactured by using cross-coupling reactions over transition metal catalyst [114-118]. Palladium(II) complexes are generally used as homogeneous catalyst in case of cross-coupling reactions in environment friendly mild conditions. Thus development of Pd-based easily recoverable and recyclable heterogeneous catalysts are predominantly required for industrial applications. Along with other approaches impregnation and encapsulation have been tried for the immobilization of Pd particles [78]. But Pd leaching is a big problem for this types of catalysts. Thus, the improvement of Pd-based catalysts as actually heterogeneous remains an interesting tusk for researchers.

Furthermore, palladium containing perovskite oxides also devel-oped as efficient popular automotive three-way catalyst with expressively developed stability due to the self-reformative role of Pd [119,120]. Against such a background, Pd-loading LaFe$_{0.57}$Co$_{0.38}$Pd$_{0.05}$O$_3$ perovskite is developed for the Suzuki reactions of aryl halides with boronic acids [77]. A number of aryl halides and boronic acids combinations were affectively transformed to the analogous bi-aryls and the catalytic efficiency enhanced with tetra-*n*-butyl ammonium bromide (TBABr) addition in several difficult transformations. The reaction between 4-bromoanisole and phenyl boronic acid over LaFe$_{0.57}$Co$_{0.38}$Pd$_{0.05}$O$_3$ was taken as a model reaction for this coupling reaction and the reaction mechanism was investigated by using kinetics, microscopy, catalyst poisoning and three-phase tests [78]. On the basis of these results, it was proposed that the Pd particles first reduced to Pd^0 by aqueous alcohol solvents and trapped to a solid surface. The soluble Pd species produces by oxidative-addition of aryl halides helped the Suzuki coupling reaction in a usual way. Transmission electron microscopy (TEM) studies showed that there is no Pd black generated. Thus, low amount (2 ppm) of leached Pd particles (confirm from hot filtration test) after reaction indicated that bulk inorganic phase was recaptured the Pd^0 particles.

Furthermore, Ullmann-type condensation of different aryl halides using thiols and phenols to the analogous sulfides and

biaryl ethers could efficiently catalyze by $La_{0.9}Ce_{0.1}Co_{0.6}$-$Cu_{0.4}O_3$ perovskite catalyst [79]. Several phenolic compound could effectively couple with an aryl halide in presence of ethyl acetate and Cs_2CO_3 additives. Three Pd-loaded $Na_{2.04}Cu_{0.95}Pd_{0.05}O_4$, $LaFe_{0.57}Cu_{0.38}$-$Pd_{0.05}O_3$ and $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskites developed for Sonogashira coupling of aryl halides with alkynes is also reported [79]. $LaFe_{0.95}Pd_{0.05}O_3$ perovskite deposited CeO_2 was also reported as efficient catalyst for Sonogashira and Heck cross-coupling reactions by flow chemistry technology [80]. But the reaction time profile is very slow and controlling the byproducts formation should be enhanced catalytic efficiency.

The $Bi_{1.97}Eu_{0.03}MoO_6$ double perovskite catalyst was also reported as an effective catalyst for the formation of substituted quinolones from different aliphatic ketones and 2-amino aryl ketones at ambient temperature in water [81].

Other reactions: $LaMO_3$ (M = Mn, Fe, Co, Cr, Al) catalyst applied for the hydrogenation of substituted and unsubstituted nitrobenzene to synthesize corresponding aniline in presence of KOH promoter in 2-propanol medium [82,83]. Among the catalysts, $LaFeO_3$ showed highest catalytic activity for this hydrogenation reaction. The same group also examined the strontium loading effect in the $La_{1-x}Sr_xFeO_3$ for nitrobenzene hydrogenation and found $La_{0.8}Sr_{0.2}FeO_3$ as the best active as well as recyclable catalysts [82,83].

Spray-flame synthesized $LaCo_{0.8}Fe_{0.2}O_3$ perovskite nanoparticles catalyst used for the oxidation of cinnamyl alcohol to cinnamaldehyde in liquid phase with TBHP under mild conditions. Waffel *et al.* [84] suggested a synergistic effect of Co and Fe for the best catalytic activity. Platinum nanoparticles supported on modified solgel method synthesized $YCo_{0.3}Fe_{0.7}O_3$ catalyst selectively hydrogenated cinnamaldehyde to cinnamyl alcohol with ~95% selectivity and 100% conversion [85].

Metal-free $LaMnO_3$ perovskite was reported as an exceptionally effective oxidation catalyst for the conversion of alkyl arenes to corresponding ketones and also for the preparation of 1,1-binaphthyl-2,2-diol (BINOL) through oxidative dimerization of 2-naphthol in presence of molecular oxygen [86]. Citric acid based sol-gel route prepared crumpled nanosheets of molybdenum-doped $LaFeO_3$ ($LaMo_{0.1}Fe_{0.9}O_3$) were used for the green synthesis of naphthapyranopyrimidines from solvent-free one-pot reaction of different substituted aromatic aldehydes, 2-naphthol and barbituric acid or its derivatives [87]. The oxygen vacancy-rich mesoporous $LaMnO_3$ prepared through a modified molecular-assembly method, act as a significantly active as well as stable hydrogenation catalyst for synthesis of furfuryl alcohol from furfural with ~100% conversion and 96% selectivity. The author proposed from density functional theory calculation that the interaction of catalyst surface with catalytic substrate facilitated by the expose oxygen deficiency sites of porous $LaMnO_3$, which lead to a lower energy barrier for this hydrogenation process [88].

Conclusion

Inspite of low surface areas, structurally modified perovskite oxides show a unique catalytic efficiency for various organic reactions in liquid phase. Various porous and nano perovskite oxides prepared by different conventional methods as well as modified methods can used as catalyst for the preparation of value-added chemicals. Perovskite oxides can efficiently use as acid-base catalysts for aldol condensation, esterification, Friedel-Crafts alkylation, cyanosilylation and one-pot synthesis. However, the connection of the catalytic efficiency with acid/base properties is still not properly discussed. Alkanes, alcohols, arenes, sulfides, *etc.* can selectively oxidized to the corresponding products over precious metal-supported, oxygen deficient, hexagonal and layered perovskite oxides catalyst with O_2, H_2O_2 and *tert*-butyl hydroperoxide (TBHP) oxidants. Palladium and copper loaded multi-component perovskite oxides can also effectively catalyze Suzuki, Ullmann and Sonogashira type cross-coupling reactions. Several reactions are employed to increase the surface areas of perovskites, which subsequently increases the catalytic activities. However, the procedures complexity and inapplicability to versatile chemical compositions is the fundamental disadvantages of present synthesis methods. Thus a simple, efficient synthesis methods are still required for synthesis of various perovskite oxides with enhanced surface areas (≥ 100 m^2 g^{-1}) at mild condition. Furthermore, elucidation of proper reaction mechanisms along with the connection of catalytic efficiency of perovskite oxides with the substrate activation modes have to be properly clarified. Therefore, appropriate explanation of the mechanistic data can lead to develop efficient perovskite oxide catalysts with proper composition for different organic reactions in the liquid phase under mild reaction conditions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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