

A Review on Perovskite as a Catalyst

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Abstract—Majority of catalysts used in the industry today are mixture of metal oxides. Preparation techniques of mixed metal oxides able to perform complex functions are of growing interest in the field of heterogeneous catalysis today. Carrying out a wide range of catalytic reactions requires catalyst with poly-functional attributes; good solid state, surface and morphological properties. Extensive background knowledge in solid-state kinetics is required in the field of heterogeneous catalysis so as to design catalyst in the engineering field. Among the mixed metal oxides, perovskite-type oxides remain prominent. The perovskite oxides have the general formula ABO_3 . The diversity of properties that these compounds exhibited is derived from the fact that around 90% of the metallic natural elements of the Periodic Table are known to be stable in a perovskite-type oxide structure. An ideal perovskite structure must adhere to the tolerance factor limits which have been investigated using a case study of the cobalt metal in the *B*-site in the paper. The tolerance factor has been calculated for the rare earth metal series and alkaline earth metal series with lanthanum, cerium, neodymium, samarium, and calcium all forming stable perovskites.

Keywords: Catalyst; Perovskite; Tolerance factor; lanthanide series.

1. INTRODUCTION

Mixed metal oxides possessing the structure and composition of the perovskite have been attracting interests from researchers [1]. This is because they exhibit fantastic solid-state properties. Perovskite is a mineral name that represents any mixed metallic oxide with the structure of calcium titanium oxide ($CaTiO_3$). It is represented with the general formula ABO_3 or A_2BO_4 , where A represents a rare earth metal (La,Ce,Pr) or alkaline earths metal (Cs, Sr, Ba,Ca) while B represents transition metals (Co,Fe,Cu,Ni, Mn, Cr, Al) [2, 3]. These minerals have a wide range of industrial, scientific and commercial importance can be obtained naturally or synthetically [4]. Labhasetwar et al., [5] attributed this importance to its affordability, high thermal stability and stoichiometric flexibility. The ability of the metals (cation) to exist in a non-stoichiometric form with oxygen (anion) can be of advantage in achieving high catalytic activity and good multifunctional properties of the perovskite catalyst. Perovskite fulfil the stability requirements for reforming reactions and also form well dispersed and stable metal particle catalysts [6, 7]. Perovskite oxides have been used as catalyst for different reactions. The ideal structure is cubic however this changes depending on the type of A and B cations employed [1]. It was found that the B-site element was responsible for its high catalytic activity [8]. Also the partial substitution of the A-site by various cations can change the oxidation state and enhance structural defects, such as anionic or cationic vacancies [9]. This leads to the A-site substituted perovskite-type catalyst showing reasonable electronic conductivity and ionic conductivity at increased or high temperatures. The partial substitution of the B-site can improve the structural stability and catalytic behaviour of the perovskite catalyst. The catalytic activity of perovskite oxide can also be improved by partial substitution of A and/or B sites with little changes in the structure [10]. In this paper, the ideal and non-ideal perovskite has been investigated using the cobalt metal in the B-site of the perovskite structure. The investigation was carried out using the Goldschmidt tolerance factor with the A-site; alkaline earth metals and lanthanides series. Also the various preparation methods used by various researchers have been reviewed.

2. PEROVSKITE PROPERTIES

A. Perovskite Structure

An ideal Perovskite has a cubic structure, with an octahedral configuration of oxygen atoms at each corner around the B atom. However, the structure of Perovskite makes it possible for the compound to allow for non-stoichiometry and partial substitution [4, 5]. Varying *A* and *B* will allow for a change in the resulting structure from the ideal structure. The change will be as a result of the properties of *A* and *B* site i.e. (ionic radius, valency and negativity of the electron) [4]. Control of the substitution carried out in the *A* and *B* site is important in changing the properties of the perovskite oxide. A careful design has to be carried out in other to bring in other elements into the Perovskite oxide. When non-stoichiometric substitution is carried out on the perovskite catalyst, oxygen conductivity is induced by oxygen valences [4].

B. Catalytic Properties

The catalytic nature of Perovskite based catalyst depends on the properties of *A* and *B* and their oxidation states. Component *A* and *B* are cations while O which is oxygen is an anion [2]. Perovskite with higher surface area are desired for catalytic and adsorption related studies. Recent studies have focused on producing perovskite at lower calcinations temperature in other to improve the porosity. Perovskite oxide calcinated at lower temperature yields higher surface area with smaller particle size [5]. The stability of the Perovskite is enhanced by the *A* cation used while catalytic behavior (activity) of the Perovskite is determined by the *B* cation [2]. Perovskite oxides exhibit a range of stoichiometries and crystal shapes, therefore because of this properties they allow for about 90% of metallic elements of the periodic table to accommodate the *A* or/and *B* positions of the oxides [3].

C. Physical Properties

The physical properties of perovskite oxides are dependent on the method of preparation applied. Perovskites are produced at high temperature and generally solid-state synthesis method is commonly utilized to prepare perovskite in pure form due to availability of impurity-free precursor. This method is suitable for perovskite used for electronic and electrical applications but fails for surface related studies [5].

3. PREPARATION METHODS

Various methods exist for perovskite preparation which have been outlined for several studies [2]; Co-precipitation, sol-gel citrate, combustion synthesis, reactive grinding, citric acid ligated, flame pyrolysis, impregnation, ultrasonic assisted incipient wetness impregnation, malic acid, solid state reaction. However, Co-precipitation method, solution combustion method, and citrate sol-gel method have been outlined as the major methods for preparing perovskite for catalytic studies [5].

A. Co-precipitation Method

Screen [4] described the co-precipitation method as the precipitation from soluble precursors of the component metals in a suitable solvent followed by solvent removal and heat treatment. This method gives a perovskite with moderate surface.

B. Combustion Method

In the combustion synthesis method described by Labhasetwar et al., [5], the ignition of the combustible components provides the fuel for the perovskite formation. They stated that in this technique, an exothermic chemical reaction between a metallic salt and a suitable organic fuel occurs in quick succession. The mixture of the reactant needs heating up to a temperature that is lower than the actual phase formation temperature. The technique produces very fine crystal powder, without decomposition or calcinations step. It is adequate for production of nano-size particle catalyst. The important step that controls this procedure is the production of self-sustaining heat by localized temperatures that is sustained for a very short time enough to cross the activation energy barrier for the formation of the perovskite phase [5]. In this process a large amount of gas is produced and this results in the formation of a foamy mass with smaller particles size and rough surface area which gives better yield in catalytic application. A short fall of this process is the gas emissions released during the synthesis as studies have not been carried out to determine if it is suitable for commercial production of perovskite.

C. Citrate Sol-gel Method

In the Citrate sol –gel method the sol gradually leads to formation of gel-like diphasic system (having both liquid and solid phase). The calcination of the dried gel precursor material gives the perovskite material. Shabbir, Qureshi, and Saeed [11] reported a novel sol-gel method for preparing nano-sized perovskite LaFeO_3 by thermal decomposition of the gel complex the nature of the substituting components was found to affect the surface area of the perovskite oxide. Oxide sintering was described by Labhasetwar et al., [5] as heating the powder of components at very high temperature.

4. CHARACTERIZATION OF PEROVSKITE

The textural and crystal structure of perovskite oxides can be characterized using measurements such as N_2 physisorption isotherms, XRD, FT-IR, TGA, CO_2 -TPD, NH_3 -TPD, H_2 -TPR, and SEM-EDX [3]. The characterization is carried out to determine the physicochemical properties of the synthesized perovskite catalyst pre and post reaction. N_2 physisorption isotherms determines the textural properties of catalyst, x-ray diffraction (XRD) shows the crystalline phase of the catalyst, fourier transform infrared spectroscopy (FT-IR) identifies the functional group, thermogravimetric analysis (TGA) shows the solid state phase change of the as-synthesized material (TPC) and carbon deposited on the catalyst surface after reaction (TPO), temperature programmed desorption (TPD- CO_2 and TPD- NH_3) determines the basicity and acidity of the perovskite respectively, temperature programmed reduction (TPR) shows the perovskite reducibility, scanning electron microscope (SEM) shows the morphology while the electron dispersion x-ray (EDX) shows the catalyst composition.

5. MERITS AND DEMERITS OF PEROVSKITE

The high catalytic activity, stability, cost effectiveness and selectivity are some of the reasons for the increase in the utilization of perovskite in reactions of environmental and commercial importance [2]. However a major setback in the use of perovskite is the low surface area of the catalyst. Perovskite is a combination of two or more simple oxides with high melting point [3].

6. IDEAL AND NON-IDEAL PEROVSKITE

In combining this two metals, A is the larger cation with minimum size limit of $r_A = 0.09\text{nm}$ and B the smaller cation with minimum size limit of $r_B = 0.051\text{nm}$ [3]. Goldschmidt introduced a factor in selecting a proper combination of A and B. The range $0.75 < t < 1$ must be strictly adhered.

where;

$$t = \frac{(r_A + r_O)}{\{\sqrt{2}(r_B + r_O)\}}$$

Tolerance factor of the perovskite oxide (t), and r_A, r_B, r_O are the radii of the ions [3, 5]. In cases where the tolerance factor is not adhered to there would be destruction of the matrix structure of the perovskite. A case study has been carried out using a transition metal; cobalt, with ionic radius of 0.0545 nm. The lanthanide metal series and alkaline earth metals were employed to determine the tolerance factor. The results obtained for the series is shown in Table 1. Lanthanum, cerium, neodymium, samarium, and calcium all showed tolerance factor within the acceptable range. However, tolerance factor of praseodymium, promethium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, beryllium, magnesium, lithium and francium could not be determined as they were seen to have no known ionic radius within the required co-ordination for combination. Strontium, barium, radium, sodium, potassium, rubidium, and caesium all had tolerance factor greater than 1. These groups are more likely to form non-ideal perovskite with unstable structures.

7. CONCLUSIONS

Catalyst design in the engineering field has led to the increasing growth of the use of mixed metal oxide of which perovskite oxides are prominent. The need to carry out a wide range of catalytic reactions requires catalyst with good solid state, surface and morphological properties. Therefore, the need to synthesize an ideal perovskite can be effectively managed using the tolerance factor. An ideal perovskite should have tolerance factor between 0.75 and 1.0. A case study carried out in this paper using the alkaline earth metals and lanthanides series on cobalt as the B-site of the perovskite structure showed that lanthanum, cerium, neodymium, samarium and calcium all formed a stable perovskite with cobalt and hence have tolerance factor within the accepted range.

Table 1: Tolerance factor using cobalt as *B*- site metal and lanthanide series

S/No.	Compound	Ionic Radius (r_a) in nm	Ionic Radius (r_b) in nm	Ionic Radius (r_o) in nm	Tolerance Factor
1	lanthanum	0.136	0.0545	0.14	1.00
2	cerium	0.134	0.0545	0.14	1.00
3	praseodymium	-	-	-	-
4	neodymium	0.127	0.0545	0.14	0.97
5	promethium	-	-	-	-
6	samarium	0.124	0.0545	0.14	0.96
7	europium	-	-	-	-
8	gadolinium	-	-	-	-
9	terbium	-	-	-	-
10	dysprosium	-	-	-	-
11	holmium	-	-	-	-
12	erbium	-	-	-	-
13	thulium	-	-	-	-
14	ytterbium	-	-	-	-
15	lutetium	-	-	-	-
16	beryllium	-	-	-	-
17	magnesium	-	-	-	-
18	calcium	0.134	0.0545	0.14	1.00
19	strontium	0.144	0.0545	0.14	1.03
20	barium	0.161	0.0545	0.14	1.09
21	radium	0.17	0.0545	0.14	1.13
22	lithium	-	-	-	-
23	sodium	0.139	0.0545	0.14	1.01
24	potassium	0.164	0.0545	0.14	1.11
25	rubidium	0.172	0.0545	0.14	1.13
26	caesium	0.188	0.0545	0.14	1.19
27	francium	-	-	-	-

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