Review- Reactive Grinding: A Noble Method for Perovskite Synthesis

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Abstract- **The adverse effects of air pollution should be taken as a serious issue. Catalytic convertors are fabricated to control the autoexhaust emission from vehicles. Perovskite substituted by noble metals are a promising alternative to control the emission of poisonous gases into the atmosphere. The limitation of the conventional methods used for preparing of perovskite is it provides low surface area and it requires high temperature and huge quantity of water which makes it very expensive. This review paper explains the use of new technique Reactive Grinding for preparation of perovskite at room temperature in a high energy ball mill which overcomes the limitations of conventional methods.**

Keywords- Catalytic convertor; Perovskite; Reactive Grinding; High energy ball mill.

I. INTRODUCTION

With increasing industrialisation and rising traffic, the air pollution is creating an adverse effect on health of all living organisms and environment. Automotive exhaust emissions are considered to be the main culprit behind the increasing levels of air pollution. Automobiles are the main source of transportation and the number of vehicles manufactured yearly is increasing exponentially. The commonly used fuels are crude oil derivatives like gasoline, petrol, diesel, kerosene etc. Other fuels that are used are LPG (Liquefied Petroleum Gas), CNG (Compressed Natural gas), hydrogen, biodiesel and others. Ideally, a combustion engine operates at the stochiometric ratio of air to fuel of 14.7 on weight basis for gasoline based fuel engines expecting a complete combustion with carbon dioxide, water vapour and nitrogen as the products. But the combustion is incomplete yielding poisonous gases like CO, HC, and NOx which are released into the atmosphere causing air pollution.

II. PEROVSKITE

Perovskite is a metal oxide having a well defined structure similar to $CaTiO_3$ (Calcium Titanate). The general formula is $AB0_3$. Here, A is the larger cation and B is the smaller one and O is the anion bonded to both the cations. The larger cation A which is surrounded to twelve oxygen in a dodecahedral structure can be rare earth, alkali or alkaline metals like Pb^{+2}, Bi^{+3} while cation B is usually 3d,4d or 5d transition metal and is surrounded by six oxygen atoms forming an octahedral structure. In a unit cell of a pervoskite, if B occupies the body centre then oxygen ion occupies the face centre and A occupies the corners of the unit cell. While if cation A is at the body centre, oxygen ion are at the middle of the edge and B in the corner of the unit cell.

Multi component Perovskite synthesized by partial substitution of the cation A and B which exhibit notable catalytic characteristics. It enhances the activity of oxidation of CO, combustion of CH_4 and conversion of NO to less harmful gases. The partial substitution of cation A and B by other metal of lower or higher oxidation state enhances the catalytic activity [1].

Due to wide range of properties and compositions, perovskite has found an area of application in many important fields like solid state chemistry, separation membranes, fuel cells, chemical sensors etc.

A. Limitations of Conventional methods

Perovskite are mainly prepared by ceramic and wet chemical methods. These methods require high calcination temperature for formation of crystalline phase and to remove organic precursors. But higher temperature leads to reduction in surface area hence decreasing the catalytic activity. To improve the surface area, lower calcination temperature is required which does not ensure proper crystalline phase formation. Moreover, wet chemical methods such as sol-gel, co-precipitation are complicated and require reagents which are expensive and also use a large amount of water well as formation of large amount of gaseous and liquid wastes which add to environmental pollution. Some methods also require complex equipment due to their method of producing the perovskite. To improve the surface area, the perovskite are wash coated on alumina. But several perovskite compositions and their precursors are reactive to alumina and hence cannot be used in all the cases. Due to these limitations of conventional methods of preparing perovskite, researches have proposed a new method called Reactive Grinding. This method prepares pure crystalline perovskite at ambient temperature without using the thermal treatment and also providing with high surface area of $100 m^2/g$ thus reducing the cost and providing higher efficiency [2]-[4].

III. REACTIVE GRINDING

Mechanochemical processing is a powder processing technique. Here, chemical reaction and phase transformation take place due to high intensity milling due to application of mechanical energy. Due to severe mechanical action on the solid surface, chemical and mechanical changes take place [5]-[7]. The mechanical energy is converted to chemical energy which causes the reaction which commonly occurs at higher temperatures. This method is used to synthesis metal oxides, carbides, nitrides and nanosized particles. The materials prepared by this method are used in electrochemistry, catalysis, absorbers etc.

Reactive grinding involves synthesis of material by high energy ball mills e.g. Planetary ball mill, SPEX shaker mills, attritor mills in which salt precursors are milled and high energy is induced due to intense milling causing chemical reaction to occur. The powder particles undergo cold welding, fracturing and rewelding. Process control agents (PCA) can be added to minimize cold fracturing of powder particle among them. The powder particle is milled for a specific duration until a steady state is reached [8]. Metal powder material are milled using a liquid medium, it is called wet grinding. Here, the liquid only facilitates milling but does not take part alloying to the powder. If no liquid is involved, it is called dry grinding [9], [10].

Types of milling equipments

The commonly used milling equipments are discussed below. These vary in design, capacity, efficiency, cooling and heating provisions and so forth.

A. Planetary ball mill

In this mill, a few hundred grams of powder can be milled at the same time. It shows a planet like motion along its vial and so is named planetary ball mill. It is placed on a supporting rotating disc and the drive mechanism rotates along its axis. The material and the metal balls are grounded by the centrifugal force produced due to the motion of the vials rotating along their own axis and that produced by the rotating disc, which are opposite in nature. The difference in speed of rotation of grinding jar wall and balls, results in strong frictional forces acting on the sample. Coriolis forces acts on the balls and displace them from the grinding jar wall. The ball moves to the opposite side of the jar causing an impact on the material and grinding occurs. It releases considerably high dynamic impact energy. The combination of frictional and impact energy causes high degree of size reduction of material in a planetary ball mill [10].

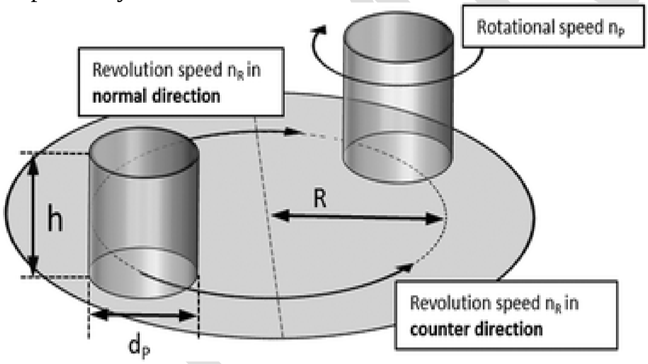

Figure 1. Planetary ball mill [12]

B. SPEX Shaker mills

These mills can mill about 10-20g of material at a time and are commonly used in laboratory investigation [11] .The commonly used version has a via which contain the material to be grounded and the grinding balls, secured in a clamp and swung energetically back and forth a several thousand times per minute. The ball velocities are high (around 5 m/s) as the amplitude (about 5cm) and speed (about 1200rpm) of the clamp are high and hence the impact force of ball is significant. Therefore, this mill can be considered high energy ball mill. The disadvantages of this equipment are: initially the ball may only roll around the vial without creating an impact which reduces the intensity of milling and second, the round ended vials are heavy while the flat ended are 30% lighter, however some powder may get accumulated in the edges and remain unprocessed [13].

C. Attritor mills

These are also known as stirred ball mills. It can mill weight of few pounds to 100lb at a time. It consists of a vertical drum which has a series of impellers in it. These impellers are rotated by a powerful motor which in turn rotates the steel balls. The impellers set progressively at right angles to each other, charge the ball. The material is subjected to forces like impact, shear, rotation and tumbling which lead to size reduction. As there is collision between balls, between balls and container walls, between balls, agitator shaft and impeller, micro ranged fine powder are produced.

D. Commercial ball mill

These are very much larger in size a used commercially; they can grind around 1250kg at a time. As the milling energy increases, the milling time decreases.

It has been observed that a process takes few minutes in a SPEX Shaker mill, will require few hours in an attritor mill and few days in commercial mill [11] .

E. Process Variables In Milling

For any process, the process variables have to be optimized to obtain the desired output. The product size is important it will depend on process variables like Type of mill, Mill container, Milling speed, size and capacity, Ball to powder ratio and others. These are interdependent.

1) *Type of mill*

Different mills have different capacity, speed of operation and capacity to control the operation by varying temperature of mill and extent of minimizing contamination of the milled powder. A suitable mill is chosen depending on the type, quantity and final constitution required.

2) *Milling container*

Due to the continuous impact force of the milling balls on the powder, some of the container material will be dislodged and incorporated in the powder and it will cause contamination the final product. So the material of the jar, vial and bowl should be properly chosen [14].

3) *Milling speed/Energy*

It is obvious that faster the mill rotates more will be the grinding of the material as more kinetic energy will be acting. However, depending on the design, maximal speed should be selected. Usually, above critical speed the balls keep rolling along the vial and do not fall down to create impact. Hence, the speed should be kept just a little lower than the critical speed so that it falls from maximum height and create maximum impact on the material.

Limitations of high speed are that it increases the temperature of the mill. It is favourable in the cases where diffusion is required to provide homogeneity but also at high temperatures, transformation processes is accelerated and decomposition of supersaturated solids or metastable phases are formed during the milling process [14] .

4) *Milling time*

Usually time is chosen such that a steady state is established between cold welding and fracturing process. Time required for milling depends on the type of mill used, final composition required, intensity of the mill, BPR, and temperature of the mill. It is noted that time required for high energy ball mil like SPEX Shaker mill is less as compared to attritor or commercial mills. Before selecting the time, a combination of all the above mentioned factors should be considered [15].

5) *Grinding medium*

It is important that the density of the grinding medium is high as it will create more impact on the material. It is favourable that the grinding medium and the mill be made of the same material so as to avoid cross contamination of the product. Hardened steel, cast iron, stainless steel, hardened chromium steel are few grinding medium materials [14].

6) *Ball to powder ratio*

A ball to powder ratio (BPR) also known as Charge Ratio of 10:1 is most commonly used. Higher BPR are used only in special cases where some certain desired properties are to be obtained or to get effects faster. Higher BPR values will grind faster but it will also increase the level of contamination in the product [16].

Other important factors are: Extent of filling the vial, Milling atmosphere, Temperature of milling and Process control agent.

IV. CONCLUSION

From the literature review, I conclude that perovskite oxides substituted by noble metals are a promising alternative for controlling the autoexhaust emission because of low cost, thermal stability at high temperatures, very good redox properties and great versatility. Further, using reactive grinding provides with higher surface area at ambient temperature and deletes the need of water and high amount of power consumption. It can be done on solvent free basis and produces large amount of nanocomposites.

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REFERENCES

[1]. Z. Villaneuva, A. H., (2006). Reduction of NO by CO over nanoscale $La_{1-x}Cu_xO_3$, J.Mol.Catal.A:Chem.
[2]. Y. Chang, J. McCarty, (1996). "Novel oxygen storage components for advanced catalysts for emission control in natural gas fuelled vehicles", Catalysis Today
[3]. B. Seyfia, M. Baghalha, H. Kazemian, (2009) "Modified LaCoO3 nano-perovskite catalysts for the environmental application of automotive CO oxidation", Chemical Engineering Journal
[4]. P. Avila, M. Montes, E. Miro, (2005), "Monolithic reactors for environmental applications A review on preparation technologies", Chemical Engineering Journal.
[5]. S. Kaliaguine, A. Van Neste, V. Szabo, J. Gallot, M. Bassir, R. Muzychuk, (2001). "Perovskite-type oxides synthesized by reactive grinding Part I. Preparation and characterization", Applied Catalysis A: General.
[6]. R. Zhang, A. Villanueva, H. Alamdari, S. Kaliaguine,(2006) "Catalytic reduction of NO by propene over LaCo1-xCuxO3 perovskites synthesized by reactive grinding", Applied Catalysis B: Environmental
[7]. R. Zhang, H. Alamdari, S Kaliaguine,(2006) "Fe-based perovskites substituted by copper and palladium for NO + CO reaction", Journal of Catalysis.
[8]. V. Szabo, M. Bassir, A. Van Neste, S. Kaliaguine(2003) "Perovskite-type oxides synthesized by reactive grinding Part IV. Catalytic properties of LaCo1−xFexO3 in methane oxidation", Applied Catalysis B: Environmental.
[9]. L. Wang, Y. Liu, M. Chen, Y. Cao, H,Yong, W. Gui-Sheng , W. Dai, K. Fan,(2007) "Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis", Journal of Catalysis
[10]. A. Bellosi, F. Monteverde, S. Botti, S. Martelli, (1997) "Development and Characterization of Nanophase Si3N4-Based Ceramics", Material science forum.
[11]. G. Nicoara, D. Fratiloiu, M. Nogues, J.L. Dormann, F. Vasiliu,(1997) "Ni-Zn Ferrite Nanoparticles Prepared by Ball Milling", Material science forum
[12]. H. Mio, J. Kano, F. Saito,(2009) "Scale-up method of planetary ball mill", Chemical Engineering Science
[13]. C. Suryanaryan, Mechanical Alloying and Milling, Marcel Dekker New York, Chapter 4.
[14]. K. Venkataraman, K. Narayan,(1998). "Energetics of collision between grinding media in ball mills and mechanochemical effects", power technology.
[15]. S. Tadier, N. Bolay, C. Rey, C. Combes,(2010). "Co-grinding significance for calcium carbonate–calcium phosphate mixed cement. Part I: Effect of particle size and mixing on solid phase reactivity", Acta Biomaterialia
[16]. K. Miklos, D. Beke,(1996). "Phase Transitions in Cu-Sb Systems Induced by Ball Milling", Material Science Forum.