



## **A Brief Review on Heterogeneous Catalytic Oxidation of Nitric Oxide**

Sunaina Sharma<sup>1</sup>, Siva Prasad Das<sup>1,\*</sup>

<sup>1</sup>*Department of Chemistry, University Institute of Science, Chandigarh University, Mohali, Punjab 140413, India*

*\*Correspondence: Dr. Siva Prasad Das, Email: [siva.spd@gmail.com](mailto:siva.spd@gmail.com)*

### **Abstract**

This review is designed about the current improvements on catalysts and their catalytic performances on oxidation of nitric oxide (NO). Nitric oxide is produced from stationary as well as mobile sources which is one of the major pollutants that can cause problems and harms the environment like ozone layer depletion, photochemical smog, acid rain, etc. Due to these ongoing environmental concerns, several methods have been developed for its elimination. Oxidation of nitric oxides in the presence of catalysts is considered as a key step for the removal of this pollutant. Over the years, various types of catalysts are developed for the oxidation of NO which may be categorized as carbon-based catalysts, supported catalysts, multi metal oxides and perovskite catalysts. We are discussing their properties and catalytic performances category-wise herein.

**Keywords:** Nitric oxide, heterogeneous catalysis, pollution, catalytic oxidation.

### **1. Introduction**

With the advancement of catalysis, now-a-days, a wide variety of challenging chemical reactions operated smoothly. This is a process in which the rate of chemical reaction changes by the use of catalyst. Catalyst does so by lowering the activation barrier to complete the reaction in a faster rate.<sup>1,2</sup> The main motive of the use of catalyst is to accelerate the rate of chemical reaction. Catalysis is broadly divided into two types, viz. homogeneous catalysis and heterogeneous catalysis. In homogeneous catalysis, the catalysts, reactants and products are all in same phase. The major drawback of this method is that the catalysts have short life and regeneration of catalysts may or may not be feasible.<sup>3</sup> In heterogeneous catalysis, reactants or products and catalyst are in different phase. The use of heterogeneous catalysis offers selective product formation, easy recycling of the catalyst, faster reaction and avoidance of the formation of unwanted products.<sup>4,5</sup> Due to these advantageous aspects, heterogeneous catalysis is widely used in different chemical transformations.

Nitric oxide composed of one atom of nitrogen and one atom of oxygen and is a colourless gas having formula NO and is a free radical due to the presence of unpaired electron.<sup>6, 7</sup> In biological system, formation of nitric oxide is done by enzyme called nitric oxide synthase which is obtained from L-arginine.<sup>8, 9</sup> Apart from this, due to the growth of the automobile industry, the combustion of fuel is increased tremendously which produces enormous amount of NO that is harmful for the environment as well as for the health of human beings.<sup>10-12</sup> Thus, the compound, NO is considered as a pollutant. Along with the automobile sources, NO is also produced from the stationary sources like coal-fired power plants, industry, etc.<sup>13-15</sup> The NO produced from stationary as well as mobile sources can cause many problems such as photochemical smog, acid rain, ozone layer depletion, etc. which are harmful for the environment and causes various health hazards.<sup>16, 17</sup> To reduce the harmful effect of NO on environment and humans various techniques are introduced by different-different researchers such as NO<sub>x</sub> storage-reduction (NSR), continuously regenerating trap (CRT), three-way catalysis, and selective catalytic reduction of NO<sub>x</sub> (SCR).<sup>18,19</sup> In NSR process, NO is oxidized to NO<sub>2</sub> over the catalysts. In CRT process, NO is first oxidized to NO<sub>2</sub>, which further oxidizes and collected on a diesel particulate filter. Among SCR processes, which is used for removal of NO basically from stationary sources, NH<sub>3</sub>-SCR method is important for the efficient removal of NO<sub>x</sub> emission.<sup>18, 19</sup> In this technique, selective catalytic reduction of NO is done with the help of NH<sub>3</sub>.<sup>20</sup> Due to high activity of NO reduction and less sensitivity for sulphur poisoning, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> were commonly used in NH<sub>3</sub>-SCR catalysts.<sup>21, 22</sup> CeO<sub>2</sub> and MnO<sub>x</sub> are also used as SCR catalysts because CeO<sub>2</sub> shows redox properties and MnO<sub>x</sub> is used as low temperature SCR catalyst.<sup>23</sup> Thus it is realized that by choosing suitable catalysts, the catalytic oxidation of nitric oxide can be done efficiently and it is regarded as the useful remediation for the removal of harmful effect of NO.

In this review, we are discussing the synthesis, properties and performances of different types of catalysts used in the oxidation of NO. We have classified the catalysts in this review by dividing them into four types, viz. Carbon-based catalysts, Supported catalysts, Perovskite catalysts and multi-metal oxide catalysts. Supported catalysts are further divided into noble metal and multi-metal catalysts.

## 2. Different NO Oxidation Catalysts

### 2.1. Carbon-based catalysts:

Carbon-based catalysts have been considered as better catalysts for NO oxidation. It is cost-effective as well as good for the removal of NO<sub>x</sub>. Among carbon-based catalysts, two are popular viz activated carbons (ACs) and activated carbon fibers (ACFs). These carbon-based catalysts have adsorption, acid site and also having the catalytic and redox properties.<sup>24-27</sup> The most advantageous aspect of AC is its ability to oxidize other pollutants, such as SO<sub>2</sub> to SO<sub>3</sub> or elemental mercury to ionic mercury, in addition to NO.<sup>28</sup> Guo et al.<sup>29-30</sup> reported three AC and ACF based catalysts viz polyacrylonitrile-ACF, coconut-AC and pitch-ACF for the catalytic oxidation of NO to NO<sub>2</sub> at room temperature (30°C) from flue gases. The NO conversions were reported to be about 81-95%, 44-75% and 25-68% for coconut-AC, pitch-ACF and PAN-ACF, respectively, shown in Fig 1. Coconut-AC was found to be the best catalyst. It was also reported that increase of O<sub>2</sub> concentration, helps in NO oxidation. But NO conversion decreased sharply with the increase in temperature and humidity, surprisingly when the temperature reaches at 100°C and relative humidity is 15%, ACs and ACFs were totally inactivated. Adapa et al.<sup>31</sup> reported ACF based catalysts derived on various precursors such as pitch-based, phenolic resin and viscose rayon. They studied their activity in a packed bed tubular reactor under varying reaction temperatures (30-80°C) and concentrations of NO (100-400 ppm) and O<sub>2</sub> (5-100%). Phenolic resin-based ACF was found to be the best catalyst and maximum conversion was reported at 30°C. It was also reported that on increasing the O<sub>2</sub> concentration, NO conversion increases. The proposed catalytic pathway for the NO oxidation is shown in Fig. 2. Shen et al.,<sup>32</sup> reported that instead of ACFs, Langmuir-Hinshelwood(L-H) and Eley-Rideal(E-R) mechanism are preferred for NO oxidation pathways, during which NO<sub>2</sub> is formed by the reaction of NO<sub>3</sub> intermediate which is generated from double adsorbed NO<sub>2</sub> with NO. Dissociated oxygen that has been activated by carbon reacts with adsorbed NO in the L-H mechanism, on the other side gaseous O<sub>2</sub> can directly react with NO adsorbed in micropores in the E-R mechanism. Mochida et al.<sup>33</sup> reported the catalytic oxidation of NO to NO<sub>2</sub> over pitch-based activated carbon fibers. They found that heat treatment, i.e., treatment of the fibers at 850°C, significantly improved the conversion of NO to 87% in dry air, 62% in air with 80% relative humidity and 24% in wet air at 25°C in pitch-based activated carbon fibers. Mohsen et al.<sup>34</sup> reported the activity of hydrophobic hyper-crosslinked polymers as catalyst for the oxidation of NO. They used two copolymers viz, hyper-crosslinked (XAD16N, XAD4) and low crosslinked (V493 & V503). XAD16N and XAD4 have the same BET surface area whereas V493 has more basic surface area than the V503. Hyper crosslinked polymers show better activity as compared to low-hyperlinked. XAD16N achieved 16% NO conversion at surface area of 785m<sup>2</sup>/g whereas

XAD4 shows 13% NO conversion at surface area of 810 m<sup>2</sup>/g in dry conditions. Similarly, V493 and V505 achieved 48% and 43% NO conversion at 1340 m<sup>2</sup>/g and 1050 m<sup>2</sup>/g surface area, respectively (shown in Table 1). Shirahama et al.,<sup>35</sup> reported the extended kinetics of NO oxidation over a pitch based ACF with a very large surface area. The reaction involves the adsorption of NO on the catalyst surfaces and the surface reactions leads to the formation of NO<sub>2</sub>. They proposed that the large surface area of the pitch-based ACF provides numerous active sites where NO molecule can adsorb. Subsequently, the adsorbed NO molecule undergoes surface reaction with oxygen and leads to the formation of NO<sub>2</sub>. The activity can be influenced by the ACF's surface chemistry and preparation method of the catalyst. Sousa et al.,<sup>36</sup> reported the oxidation of NO over a series of modified nitrogen doped activated carbon catalyst. The NO conversion was reported to vary between 50 and 88%. Among the modified activated carbons, the nitric acid and melamine treated were reported to be the most active for NO oxidation. It was observed that the incorporation of nitrogen into the activated carbons significantly improves the catalytic activity.

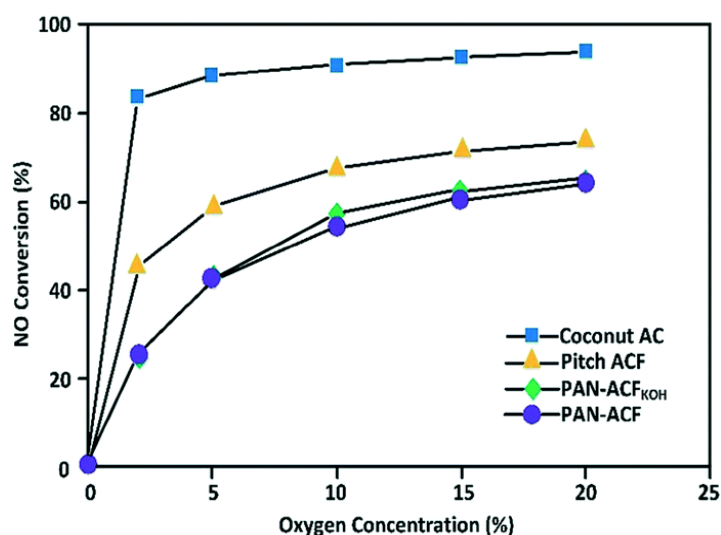


Figure 1: Oxygen concentration versus NO conversion by different carbon-based catalysts at 30 °C.<sup>29</sup>

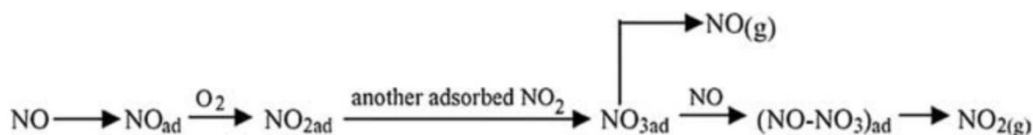


Figure 2: Catalytic pathway for the NO oxidation.<sup>31</sup>

Table 1: Summary of the NO conversion by different carbon-based catalysts.

| Carbon-based catalysts     | Surface Area m <sup>2</sup> /g | NO Conversion (%) | References |
|----------------------------|--------------------------------|-------------------|------------|
| Coconut-AC                 | 1200                           | 81-94%            | 30         |
| PAN-ACF                    | 700                            | 25-68%            | 30         |
| Pitch-ACF                  | 1000                           | 44-75%            | 30         |
| Phenolic resin-based ACF   | 1500                           | 90%               | 31         |
| Pitch-based ACF            | 800                            | 87%               | 33         |
| XAD16N                     | 785                            | 16%               | 34         |
| XAD4                       | 810                            | 13%               | 34         |
| V493                       | 1340                           | 48%               | 34         |
| V503                       | 1050                           | 43%               | 34         |
| Pitch-based ACF            | -                              | 75%               | 35         |
| AC-M & AC-HNO <sub>3</sub> | 1450 & 1225                    | 88%               | 36         |

## 2.2. Supported catalysts:

In supported catalysts, the active site is present on the surface of catalysts where the catalytic oxidation reaction takes place.<sup>37</sup> The metal component of a supported metal catalyst is typically a transition metal such as platinum (Pt), palladium (Pd), gold (Au), nickel (Ni), or copper (Cu). These metals are chosen based on their catalytic activity, selectivity, and resistance to deactivation under typical reaction conditions. The metal nanoparticles are dispersed on the support material through various methods, including impregnation, deposition-precipitation, and co-precipitation.

### 2.2.1 Noble metal catalysts:

The most common noble metal catalyst for the NO oxidation is platinum (Pt). Platinum is chosen because of its life span and its superior activity in NO oxidation. The factors on which the NO oxidation activity depend are the types of support, Pt dispersion, formation of platinum oxide and Pt loading.<sup>38</sup> Li et al.<sup>39</sup> reported the activity of platinum support on TiO<sub>2</sub> for NO oxidation. The catalysts were prepared by photo-deposition of platinum onto TiO<sub>2</sub> supports. In-situ FTIR spectroscopy was used to analyse the surface species produced during NO oxidation under different reaction conditions (absence/presence of SO<sub>2</sub>) over the Pt/TiO<sub>2</sub> catalyst. Fig. 3 depicts the catalytic activity for NO oxidation on TiO<sub>2</sub> and Pt/TiO<sub>2</sub>. TiO<sub>2</sub>

support has a low NO oxidation activity (20%) in the presence and absence of SO<sub>2</sub>, implying that the high NO oxidation activity of Pt/TiO<sub>2</sub>. The temperature effected the NO oxidation. It was seen that the supported catalyst Pt/TiO<sub>2</sub> could achieved upto 50% NO conversion at 210°C while maximum NO conversion of 94% was achieved at 250°C, in the absence of SO<sub>2</sub>. In the presence of SO<sub>2</sub>, maximum NO conversion was achieved upto 75% at 350°C. Auvray and Olsson<sup>40</sup> reported the palladium and platinum catalyst supported on alumina for NO oxidation. The catalysts were prepared by co-impregnation and sequential impregnation of the metals onto alumina supports. The NO oxidation was examined in a flow reactor over Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> or two Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts and also examined the effect of propene, water and their combination. The most effective catalyst was Pt-Pd-Seq, which achieved 91% conversion of NO at 250°C. Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Pd-CoImp have similar activity profile, whereas Pt/Al<sub>2</sub>O<sub>3</sub> was little more active as shown in Fig 4. Elguezabal et al.<sup>41</sup> reported three Au-TiO<sub>2</sub> viz Au-TiO<sub>2</sub>(0.5 wt%), Au-TiO<sub>2</sub>(1.0 wt%), Au-TiO<sub>2</sub> (3.0 wt%) and bare TiO<sub>2</sub>. These catalysts were prepared by sol-gel method by adding gold chloride (HAuCl<sub>4</sub>) to a titanium(IV) isopropoxide solution. Photocatalytic conversion of NO is shown by the catalysts in oxygen rich mixture. The NO conversion shown by catalysts as 85% by Au-TiO<sub>2</sub>(0.5 wt%), 81% by Au-TiO<sub>2</sub>(1.0 wt%), 78% by Au-TiO<sub>2</sub>(3.0 wt%) and 70% by TiO<sub>2</sub>. Au-TiO<sub>2</sub>(0.5 wt%) was found to be possess best catalytic activity (Table 2).

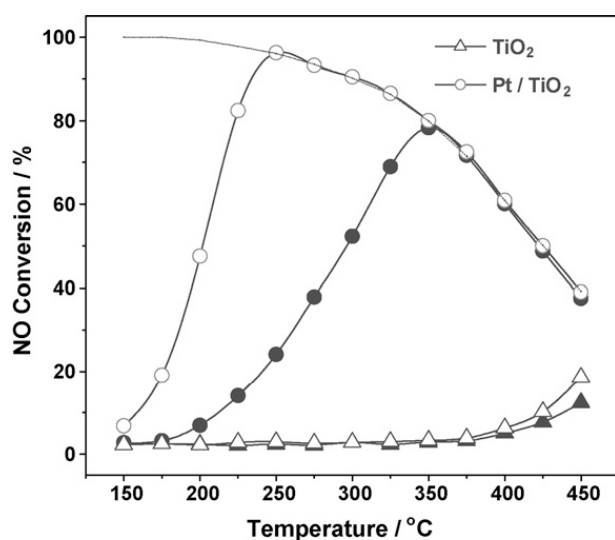


Figure 3: NO oxidation on TiO<sub>2</sub> and Pt/TiO<sub>2</sub>.<sup>39</sup>

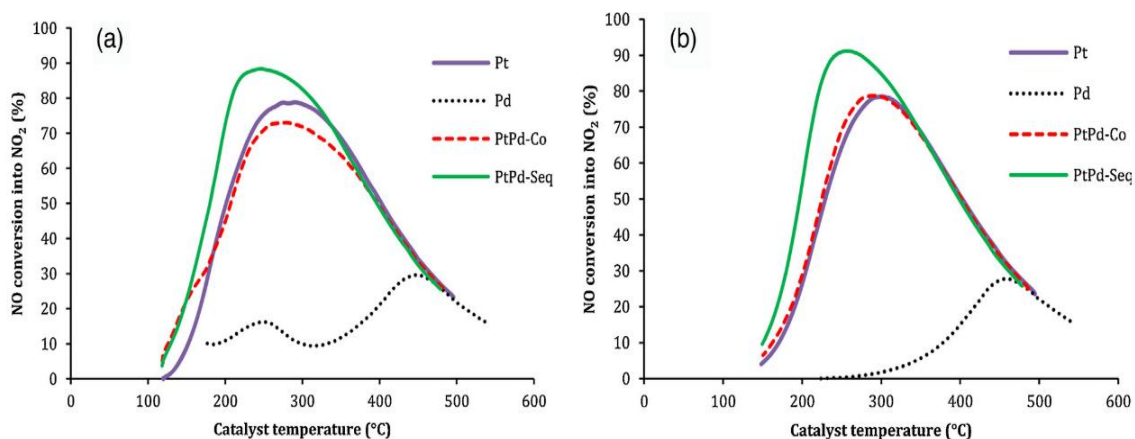


Figure 4: Comparison of the catalysts ability to convert NO into NO<sub>2</sub> with 500 ppm NO, 8% O<sub>2</sub> and Ar.<sup>40</sup> (a) Conversion during the heating phase (5 °C/min) and (b) cooling phase (-5 °C/min).

Table 2: NO conversion by different Noble metal catalyst.

| Catalysts                     | NO conversion in % | Temperature(°C) | References |
|-------------------------------|--------------------|-----------------|------------|
| Pt/TiO <sub>2</sub>           | 94%                | 350 °C          | 39         |
| PtPd-Seq                      | 91%                | 250 °C          | 40         |
| Au-TiO <sub>2</sub> (0.5 wt%) | 85%                | 300 °C          | 41         |

### 2.2.2 Metal oxides catalysts:

Metal oxides like TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> with the cobalt support provides catalytic activity of NO oxidation. Zhong et al.<sup>42</sup> reported two methods viz impregnation method and citrate complexation method for the synthesis of Zr<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub> by cobalt support. Due to high activity in oxidation processes, cobalt-based catalysts acquired greater attention and have been suggested as potential approach for NO oxidation to NO<sub>2</sub>. It has been observed that cobalt supported on a variety of supports, including TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>, is active for NO oxidation. Ceria-zirconia mixed oxides have also received a lot of attention due to their improved oxygen storage/release capability and thermal stability compared to pure CeO<sub>2</sub>. Catalyst prepared by both methods (impregnation & citrate complexation method) show high catalytic activity in NO oxidation but citrate complexation method show greater catalytic activity than impregnation method. At 300 °C almost 80% of NO conversion is achieved.

Zhao et al.<sup>43</sup> studied the sulphur resistance and hydrothermal activity of  $\text{MnO}_x/\text{ZrO}_2$  and  $\text{MnO}_x/\text{TiO}_2$  for the oxidation of NO.  $\text{TiO}_2$  acts as an inert support that primarily serves as a dispersed surface for  $\text{MnO}_x$  during NO oxidation. Due to surface bifunctionality, acidity and basicity,  $\text{ZrO}_2$  is an excellent support material that can significantly increase the activity of supported metal catalysts.  $\text{Mn}/\text{ZrO}_2$  exhibits higher activity across the whole temperature range, with a maximum NO conversion of 78% at 270 °C, whereas  $\text{Mn}/\text{TiO}_2$  has a maximum NO conversion of 59% at 298 °C.  $\text{TiO}_2$  and  $\text{ZrO}_2$  are both oxides have extremely low activity, with a maximum NO conversion of less than 20%, indicating that the support materials cannot provide active sites for NO oxidation.  $\text{Mn}/\text{ZrO}_2$  show high activity than that of  $\text{Mn}/\text{TiO}_2$  in NO oxidation (Fig 5). Zhang et al.,<sup>44</sup> reported the performance of NO oxidation at various temperatures over the  $\text{Cr}(1)\text{Ce}(X)\text{TiP}$  catalysts supported on TiP.  $\text{Cr}(1)\text{Ce}(0.25)\text{TiP} > \text{Cr}(1)\text{Ce}(0.5)\text{TiP} > \text{Cr}(1)\text{Ce}(0.17)\text{TiP} > \text{Cr}(1)\text{Ce}(0)\text{TiP} > \text{Cr}(1)\text{Ce}(1)\text{TiP}$  is the order of decreasing catalytic activity of NO conversion. The maximum NO conversion of 69% was achieved by  $\text{Cr}(1)\text{Ce}(0.25)\text{TiP}$  at 350°C (Table 3).

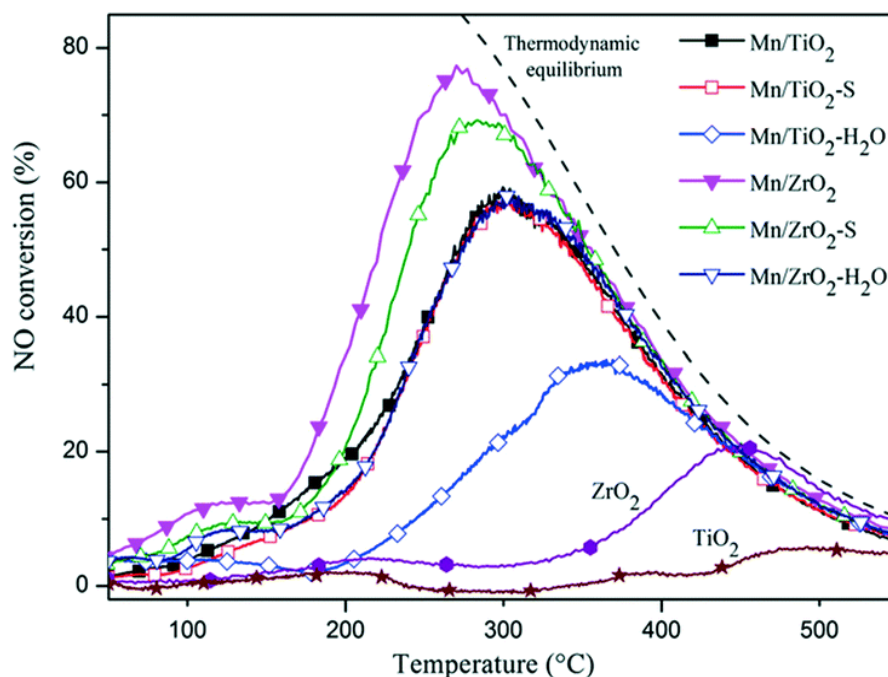


Figure 5: Catalytic NO conversion activity by  $\text{Mn}/\text{TiO}_2$  and  $\text{Mn}/\text{ZrO}_2$ .<sup>43</sup>

Table 3: NO oxidation activity by supported metals.

| Catalysts                              | NO conversion<br>in % | Temperature(°C) | References |
|--|-----------------------|-----------------|------------|
| $\text{Zr}_{1-x}\text{Ce}_x\text{O}_2$ | 80%                   | 300°C           | 42         |



|                     |     |       |    |
|---------------------|-----|-------|----|
| Mn/ZrO <sub>2</sub> | 78% | 270°C | 43 |
| Mn/TiO <sub>2</sub> | 59% | 298°C | 43 |
| Cr(1)Ce(0.25)TiP    | 69% | 350°C | 44 |

### 2.3. Perovskite catalysts:

The general form of perovskite catalysts is ABO<sub>3</sub>, in which size of A cation is bigger than B and cation A is 12-folded coordinated with oxygen whereas cation B is 6-folded coordinated.<sup>45</sup> Perovskite-type oxidation catalysts refer to catalysts that have a high degree of dispersion and uniformity of the active sites on the catalyst surface. This can be achieved through various synthesis method, such as sol-gel, co-precipitation or hydrothermal methods which can control the size, morphology and distribution of the catalyst particles.<sup>46</sup> Chen et al.<sup>47</sup> reported the catalytic activity of La<sub>x</sub>MnO<sub>3</sub> perovskite catalyst for different values of x, i.e., 0.9, 0.95, 1, 1.05, 1.15. The perovskite catalysts La<sub>x</sub>MnO<sub>3</sub> (x=0.9, 0.95, 1, 1.05, 1.15) were prepared by sol-gel method and characterized by various techniques like XPS, BET, EPR and XRD. Among all values of x, x=0.95 exhibit superior catalytic activity for NO oxidation. La<sub>0.95</sub>MnO<sub>3</sub> achieved 50% of NO conversion at 250 °C and maximum NO conversion was achieved at 296 °C which was 85%. Zhao et al.,<sup>48</sup> prepared LaFeO<sub>3</sub> catalyst by pomelo peel for the oxidation of NO. The structure and morphology were analysed by various characterization techniques including XRD and SEM. The results showed that the porous structure of pomelo peel was successfully recreated by the hierarchically porous LaFeO<sub>3</sub> perovskite with a high specific surface area. The LaFeO<sub>3</sub> perovskite prepared by pomelo peel i.e hierarchically porous LaFeO<sub>3</sub> show better catalytic activity than LaFeO<sub>3</sub> perovskite prepared without using pomelo peel under the same condition. At 313 °C, 76% of NO conversion is achieved by using LaFeO<sub>3</sub> perovskite prepared without using pomelo peel whereas maximum NO conversion of 90% at 305 °C was achieved by using LaFeO<sub>3</sub> by pomelo peel. Chen et al.<sup>49</sup> discussed the three types of perovskite catalysts viz LaMnO<sub>3</sub>, LaFeO<sub>3</sub> and LaCoO<sub>3</sub> according to their catalytic activities for the oxidation of NO. The order of activity for these three catalysts: LaCoO<sub>3</sub> > LaMnO<sub>3</sub> > LaFeO<sub>3</sub>. In NO oxidation over perovskite, active oxygen plays a critical role. After hydrothermal ageing, particularly the activity for LaMnO<sub>3</sub> and LaFeO<sub>3</sub> dropped at low temperature and the best activity was showed by LaCoO<sub>3</sub>. This deactivation was caused by a decrease in surface area and an increase in crystal size, that led to the loss of active sites. The LaCoO<sub>3</sub> showed high activity

and maximum conversion of 83% at 260 °C (Table 4). Yoon et al.,<sup>50</sup> prepared the  $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$  catalyst by using citric-acid method for the oxidation of NO and compare the activity of  $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$  with  $\text{LaMnO}_3$ . When Ag partially added for La in  $\text{LaMnO}_3$ , the NO oxidation activity raised dramatically, with the activation energy decreasing from 66.72.1 to 47.91.8 KJ/mol. Among the Ag-doped perovskites investigated in this study,  $\text{La}_{0.8}\text{Ag}_{0.2}\text{MnO}_3$  showed the highest NO oxidation activity. S Zhong et al.,<sup>51</sup> prepared a series of perovskite catalysts  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$  where  $x = 0, 0.1, 0.3, 0.7, 1.0$  by Co-precipitation method for the analysis of NO oxidation. The effect of Co substitution into the  $\text{LaNiO}_3$  on the oxidation of NO was examined. XRD,  $\text{H}_2$ -TPR and NO-TPD were used to investigate the roles of Co in the NO oxidation pathway over the  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ .  $\text{LaNi}_{0.7}\text{Co}_{0.3}\text{O}_3$  show the best catalytic activity among all  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$  ( $x = 0, 0.1, 0.7, 1.0$ ) shown in Fig 6.

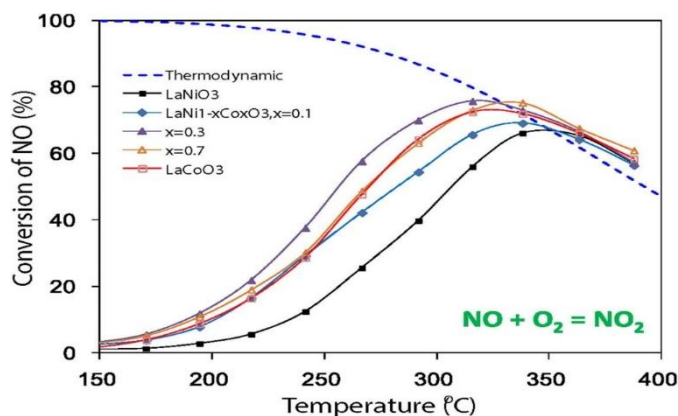


Figure 6: Catalytic activity by  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ,  $\text{LaCoO}_3$  for NO conversion.<sup>51</sup>

Table 4: Method of preparation of perovskite catalysts and NO conversion.

| Perovskite catalysts          | Method of preparation      | Conversion of NO in % | Temperature (°C) | References |
|-------------------------------|----------------------------|-----------------------|------------------|------------|
| $\text{La}_{0.9}\text{MnO}_3$ | Sol-gel method             | 85                    | 296 °C           | 47         |
| $\text{LaFeO}_3$              | Pomelo peel                | 90                    | 305 °C           | 48         |
| $\text{LaCoO}_3$              | Citric acid Sol-gel method | 83                    | 260 °C           | 49         |
| $\text{LaNi}$                 | Co-precipitation method    | 74                    | 320 °C           | 51         |

#### 2.4. Multi-metal oxide catalysts:

Multi metal oxide are a class of materials that contain two or more types of metal cations in their crystal structure. Multi-metal oxide can also provide a high surface area and porosity, which can increase the accessibility of the active sites and surface properties can be modified by doping, substitution which can improve their catalytic activity and selectivity.<sup>52</sup> Mingshan et al.,<sup>53</sup> reported  $\text{MnO}_x\text{-CeO}_2$  catalysts that have been extensively studied for the catalytic oxidation of NO. They have synthesized the  $\text{MnO}_x\text{-CeO}_2$  catalysts by using different methods such as co-precipitation, impregnation, sol-gel and hydrothermal and each method results in different catalytic properties. The catalyst synthesized by co-precipitation method showed the best NO conversion than other methods and maximum conversion of 60% was achieved at 250°C. R Guo et al.,<sup>54</sup> reported the preparation of  $\text{CeO}_x\text{-MnO}_x$  core-shell structure catalyst for the oxidation of NO which involves the deposition of Mn species onto the surface of  $\text{CeO}_2$  support. The deposition can be achieved by various methods such as impregnation, co-precipitation and hydrothermal synthesis. Compared to  $\text{CeMnO}_x$  produced using citric acid method, the catalyst  $\text{CeO}_x\text{-MnO}_x$  showed better intrinsic catalytic activity. F Lin et al.,<sup>55</sup> reported that by using sol-gel method, a series of  $\text{CeO}_x\text{-MnO}_x$  catalysts with different molar ratios of Mn/Ce can be synthesized for the catalytic oxidation of NO. Fig 7 showed the catalytic activities of  $\text{CeO}_x\text{-MnO}_x$  catalysts with different molar ratios of Mn/Ce. The catalyst with pure  $\text{CeO}_2$  (Mn/Ce=0) achieved about 60% NO conversion efficiency at 330°C. However, on the addition of the Mn to the catalyst, the catalytic activity is improved significantly. It was reported that the NO conversion efficiency of the catalyst was increased and then decreased with increasing Mn doping levels. The best molar ratio of Mn/Ce is 0.4, which shows outstanding activity in catalysing NO oxidation at low temperatures. The highest NO conversion efficiency is almost 96% at 238°C and more than 60% can be achieved at 160°C. Shen et al.,<sup>56</sup> reported two types of hollow  $\text{MnO}_x\text{-CeO}_2$  mixed oxide catalysts viz  $\text{MnO}_x\text{-CeO}_2$ (CS) and  $\text{MnO}_x\text{-CeO}_2$ (AC) and evaluated their effectiveness for NO oxidation. The result showed that  $\text{MnO}_x\text{-CeO}_2$ (CS) catalysts were more effective than the  $\text{MnO}_x\text{-CeO}_2$ (AC). The best activity was observed in  $\text{MnO}_x\text{-CeO}_2$ (CS1) catalyst, which achieved a maximal NO conversion of 82% at 220°C. Shao et al.,<sup>57</sup> reported the preparation of  $\text{MnO}_x\text{-CeO}_2$  mixed oxide catalysts using co-precipitation method and evaluated their catalytic activity for NO oxidation and resistance to low concentration of  $\text{SO}_2$ . To enhance the resistance to  $\text{SO}_2$ , metal (Fe, Co, and Ni) was added in the catalyst. The result showed that the addition of metal improved the catalytic activity and resistance to  $\text{SO}_2$ . Among the

catalysts,  $\text{MnO}_x\text{-CeO}_2\text{-Fe}$  exhibited the highest activity, achieving maximal NO conversion of 62%. Liu et al.,<sup>58</sup> investigates the effect of ozone in non-thermal plasma on manganese-cerium oxide ( $\text{Mn}_x\text{Ce}_{1-x}\text{O}_2$ ) catalysts for NO oxidation. The best catalyst was obtained by treatment with 10%  $\text{O}_2/\text{N}_2$  plasma and achieved over 80% NO conversion in the temperature range of 275-325°C (Table 5). The superior catalytic performance of the manganese-cerium oxide catalyst is primarily due to the stronger interaction between manganese oxides and ceria and the formation of a poorly crystallized Mn-O-Ce phase in the catalyst. Wenhuan et al.,<sup>59</sup> reported the preparation of  $\text{CeFeO}_x$  catalyst by using co-precipitation method. Besides,  $\text{CeO}_x$  and  $\text{FeO}_x$  catalysts were also prepared by using the same procedure. The structure of catalyst was investigated by various characterization techniques such as XPS, XRD and BET.  $\text{CeFeO}_x$  showed high catalytic activity than  $\text{CeO}_x$  and  $\text{FeO}_x$ .

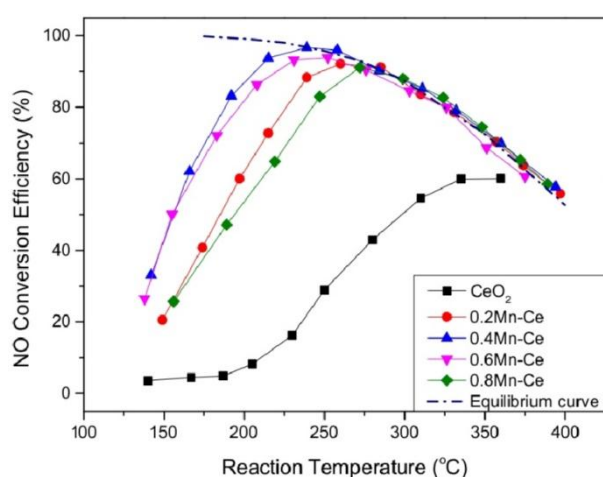


Figure 7: NO conversion efficiency of  $\text{CeO}_x\text{-MnO}_x$  with different molar ratios of Mn/Ce.<sup>55</sup>

Table 5: NO oxidation by multi metal oxide.

| Catalysts                               | NO conversion (%) | Temperature (°C) | References |
|---|-------------------|------------------|------------|
| $\text{MnO}_x\text{-CeO}_2$             | 60                | 250              | 53         |
| $\text{CeO}_x\text{-MnO}_x$             | 96                | 238              | 55         |
| $\text{MnO}_x\text{-CeO}_2(\text{CS1})$ | 82                | 220              | 56         |
| $\text{MnO}_x\text{-CeO}_2\text{-Fe}$   | 62                | -                | 57         |
| $\text{Mn}_x\text{Ce}_{1-x}\text{O}_2$  | 80                | 275-325          | 58         |

### **3. Conclusions and Future Prospective**

To remove the harmful effect of NO on the environment, catalytic oxidation of NO is done in which different catalysts are used. This review described the different types of catalysts and their performances in NO oxidation those were reported recently. Every catalyst has different properties, accordingly, some required high temperatures and some required low temperatures for their best activities. The characterization of the catalysts is also included in the review. Herein, the catalysts are grouped into four classes such as carbon-based catalysts, multi-metal oxide catalysts, perovskite catalysts and supported catalysts. The reported carbon-based catalysts viz AC and ACF have good adsorption and redox properties and are helpful in removing multiple pollutants. In supported catalysts, Pt is mostly used. However, instead of Pt, other noble metals such as Pd, Au, Ru, etc. are also used. Perovskite catalysts also played important role in oxidation of NO because of its low cost, high activity and tepid stability. Multi-metal oxides also gave better catalytic performance with high NO conversion at low temperature. Though a considerable improvement has been done in the development of NO oxidation catalysts, still lots of scope are available in it to improve the catalyst efficiency and recyclability.

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### **Conflict of Interest**

The authors announce that they don't have any conflict of interest regarding publication of the work.

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