Catalytic Oxidation of 1,2-Dichloroethane on $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) Perovskite Type Oxides

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Abstract : The toxic nature of chlorinated hydrocarbons, to humans and environment, have led scientists all over the world to make efforts to reduce emission of such harmful compounds in air. The use of noble metals and metal oxides as catalysts for oxidation of chlorinated volatile organic compounds have long been known, the drawback being their tendency to get poisoned by chlorine. Perovskites have attracted attention due to, the compositionally diverse materials that could be prepared by substitution of A- and B-site ions, which affects their ability as a catalytic material. In the present study, cerium substituted $Pr_{1-x}Ce_xNiO_3$ and $P_{1-x}Ce_xFeO_3$ (X = 0.05, 0.1, 0.2) perovskites were prepared by co-precipitation and citrate sol-gel method. The effect of increasing cerium substitution and the effect of B-site substitution (Ni/Fe) were investigated by means of XRD, BET analysis, SEM analysis and by catalytic activity evaluation. The results of analyses reveal that cerium could enter the perovskite lattice and partially occupy the position of Pr to form $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) till x = 0.1. As the doping ratio increased to x = 0.2, minor phases of cerium, nickel and iron oxides appeared along with the perovskite phase. These partially substituted perovskites demonstrated good activity for oxidation of 1,2-dichloroethane. In case of $Pr_{1-x}Ce_xNiO_3$ series the activity increased for x = 0.05 and 0.1 and decreased for x = 0.2, however, it showed linear dependence on value of 'x' for $Pr_{1-x}Ce_xFeO_3$ series. $P_{1-x}Ce_xFeO_3$ showed high catalytic activity for oxidation of 1,2-dichloroethane as compared to $Pr_{1-x}Ce_xNiO_3$.

Keywords : Perovskite,1,2-Dichloroethane, Catalytic oxidation.

Introduction and Experimental

Amongst the volatile organic compounds (VOCs), chlorinated VOC, (Cl-VOCs) are utilized as essential solvents in both industry and laboratory as degreasing compounds and as intermediates in manufacturing important commercial products. The Cl-VOCs are discharged into the environment amid manufacturing process (intermediates/finished products), sanitization process prompting dissipation, spills and other contamination released into the environment. They are of serious health concerns for both environment and human health. Other than their contribution to a dangerous atmospheric deviation, the Cl-VOCs cause exhaustion of ozone layer and have cancer-causing properties in human beings [1].

Currently, use of platinum and palladium for VOC control is constrained by cost and sensitivity of the metal to harmful chlorine/chloride by-products while oxidizing VOC [2]. Among the metal oxide, chromium oxide supported on Al_2O_3, is considered an effective catalyst [3]. However, quick deactivation was observed for the catalyst and a red deposit formed at the exit of the reactor, suggested formation of volatile red chromium oxychloride CrO_2Cl_2[4]. Due to their high oxygen storage capacity, ceria-based oxides have been found to be active in VOC oxidation. However, the catalyst had a relatively low thermal stability and deactivated in a few hours owing to strong adsorption of HCl and Cl_2[5]. A good catalyst should be resistant in the reaction conditions and limit the formation of hazardous volatile organic (phosgene, chlorinated dioxins or dibenzofurans) and inorganic (metal chlorides or oxychlorides) [6] compound. Mixed metal oxides like perovskite type catalysts are incredibly attractive for the development of environment friendly catalytic materials. They have been used in processes such as oxidation of phenol using catalytic wet air oxidation method [7], oxidation of volatile organic compounds (VOC) [8], as solid oxide fuel cells [9] and as antibacterial agents[10]. In addition to being thermally more stable, perovskites are better resistant to poisoning and are cheaper than noble metal catalysts. Partial substitution of both A- and B-sites could be carried out in perovskites leading to improved structural stability, creation of oxygen vacancies and thus exhibiting high activity for catalytic oxidation. Praseodymium based perovskites have seldom been used for oxidation of Cl-VOCs. K.Stephan*et.al*[11] employed $PrMnO_3$ for chloromethane oxidation, however , it exhibited lowest activity for the oxidation reaction. There are, however, no reports from India on the use of perovskites as catalytic materials for oxidation of Cl-VOCs.

Catalysts incorporated with Ce possess excellent oxygen storage capacity and has been reported to have several benefits as good promoter in perovskite lattice [12], enhance oxygen storage capacity [13], inhibit sintering and char formation on surface [14]. However, over 10% Ce causes segregation of CeO_2 phase leading to decrease in catalytic activity. Nickel is widely used as active site in oxidation reaction of hydrocarbons because of its selectivity with chain end but gets rapidly deactivated because of coke formation [15]. To overcome such catalyst deactivation and to enhance specific surface area, partial substitution of A-site and B-site is employed in perovskite type oxides for exploiting their catalytic properties. $La_{1-x}Ce_xNiO_3$have been employed for removal of NO_x[16], CO preferential oxidation [17] and methane reforming[18]. In all cases, the partial substitution of Ce for La showed an increase in the catalytic activity as compared to undoped $LaNiO_3$. Ce-doped perovskite was found to have higher oxidative activity for combustion of methane than pure $LaFeO_3$[19]. More recently $La_{1-x}Ce_xFeO_3$ catalysts have been examined for H_2S selective catalytic oxidation reaction[20]. The catalyst exhibited prominent catalytic activity and outstanding sulphur selectivity. However, no reports were found on the use of $La_{1-x}Ce_xBO_3$ (B = Ni/Fe) catalysts for oxidation of Cl-VOCs.

The rare earth oxide of Cerium and transition metal oxides are most feasible for industrial use due to the fact that they are cheaper than other oxides. The possibility of enhancement in perovskite properties due to Ce and Ni/Fe substitution prompted us to synthesize $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) type perovskiteoxides. In our previous work[21], the use of $PrMn_{1-x}B_xO_3$ (B= Fe, Ni, x = 0.2- 0.8) for the catalytic oxidation of 1,2-dichloroethane was reported. The high catalytic activity of $PrMn_{1-x}Ni_xO_3$catalyst was attributed to high reducibility and oxygen vacancies. The objective of present study is to investigate the effect of cerium doping, Ni/Fe substitution at B-site, preparation methods on the physical properties and catalytic activity of $Pr_{1-x}Ce_xBO_3$perovskites in the oxidation of 1,2-dichloroethane. The primordial use of these catalysts for oxidation of DCE promotes them as potentials materials for VOC oxidation.

Chemicals

The salt precursors used for the synthesis were: Pr_6O_{11} (*LobaChemie, 99.9% AR*), $Ce(NO_3)_3.6H_2O$ (99.9% AR), $Fe(NO_3)_3.9H_2O$ (*LobaChemie, 98% AR*) and $Ni(NO_3)_2.6H_2O$ (*LobaChemie, 99% AR*). To obtain the nitrate form of Praseodymium stoichiometric amounts of Pr_6O_{11} was dissolved in minimum quantity of conc. HNO_3.

Perovskite oxide synthesis

A series of $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) with x = 0.05, 0.1 and 0.2 were synthesised by co precipitation and citrate precursor sol-gel method.

Co-precipitation (CP) method

Aqueous solutions of metal nitrates in the desired stoichiometric ratio were mixed and co precipitation was carried out using 1N NaOH solution. The obtained precipitates were allowed to age for 30 minutes and then filtered. The precipitates were washed with distilled water till the solution became neutral to phenolphthalein. The filtered precipitates were dried and calcined at 800°C for 5h. The $Pr_{1-x}Ce_xNiO_3$ substituted perovskites were denoted as PCN-1, PCN-2 and PCN-3 and the $Pr_{1-x}Ce_xFeO_3$ substituted perovskites were denoted as PCF-1, PCF-2 and PCF-3 for x = 0.05,0.1 and 0.2 respectively. $PrNiO_3$ (PN) and $PrFeO_3$ (PF) were prepared in a similar manner.

Citrate precursor sol-gel (CSG) method

Aqueous solutions of metal nitrates in the required stoichiometric ratios were mixed with aqueous solution of citric acid (ratio of Metal ion: citric acid, 1:1). The solution of metal nitrates and citric acid was then heated at 90°c with stirring to evaporate most of the water resulting in the formation of gel. The gel was then placed in a preheated furnace maintained at 350°c to give formation of the black amorphous citrate precursor. The precursor was grinded and calcined at 800°C for 5h to obtain the perovskites. The $Pr_{1-x}Ce_xNiO_3$ substituted perovskites were denoted as PCN-CSG-1, PCN-CSG-2 and PCN-CSG-3 and the $Pr_{1-x}Ce_xFeO_3$ substituted perovskites were denoted as PCF-CSG-1, PCF-CSG-2 and PCF-CSG-3 for x = 0.05,0.1 and 0.2 respectively. $PrNiO_3$ (PN-CSG) and $PrFeO_3$ (PF-CSG) were prepared in a similar manner.

Characterization

Powder X-ray diffraction (XRD) pattern were recorded on a Philips X'Pert-Pro diffractometer using Cu-Kα radiation with 2θ ranging from 2°-85°. Surface area measurements using N_2 adsorption isotherm at 77K were carried out on Smartsorb-93 BET surface area analyser. The surface areas of the powdered samples were obtained by Brunauer-Emmett-Teller (BET) method. Scanning Electron Microscopy (SEM) for morphological analysis was performed on Quanta 200 SEM equipment.

Measurement of catalytic activity

The catalytic performance of all the synthesized samples was measured in a stainless-steel tubular (i.d = 12mm) fixed bed catalytic reactor (**Fig.1**) at atmospheric pressure. The catalysts were activated under a stream of N_2 at 300°C for 2h before being subjected to catalytic activity study.   0.800 g of catalyst was previously mixed with silica granules (0.2-0.8 mm) for reducing specific pressure drop across the reactor and prevent formation of hotspots. The mixture was then packed between quartz wools inside the reactor. The reactor was placed vertically (downflow vent) in the split-type furnace. The temperature of the catalyst bed was monitored by K-type thermocouple placed inside the reactor whose end was in contact with the catalyst bed. The liquid Cl-VOC was pumped into the vaporiser (also acted as a pre-mixer), which was maintained at a temperature of 200°C, to obtain a concentration of 1% vol. in air. Due to technical limitations, the reaction studies were carried out in a temperature range of 150-500°C and in absence of water in the reaction feed. After trapping the HCl and moisture the exit gases were then analysed using Shimadzu GC-2014. The effluents were analysed using the method given elsewhere[22,23]. The VOC conversion efficiency was calculated based on the following equation:

$$X_{VOC} (\%) = \frac{[VOC]_{in} - [VOC]_{out}}{[VOC]_{in}} \times 100$$

Before the data was obtained, the reaction was maintained for a period of 40 minutes at each temperature to ensure steady state conditions were attained. The analysis of by-products of the oxidation reaction was done using gas chromatography-mass spectrometry (GC-MS technique).   To determine the stability of optimum catalyst, three consecutive runs were performed, and the catalytic activities were studied.
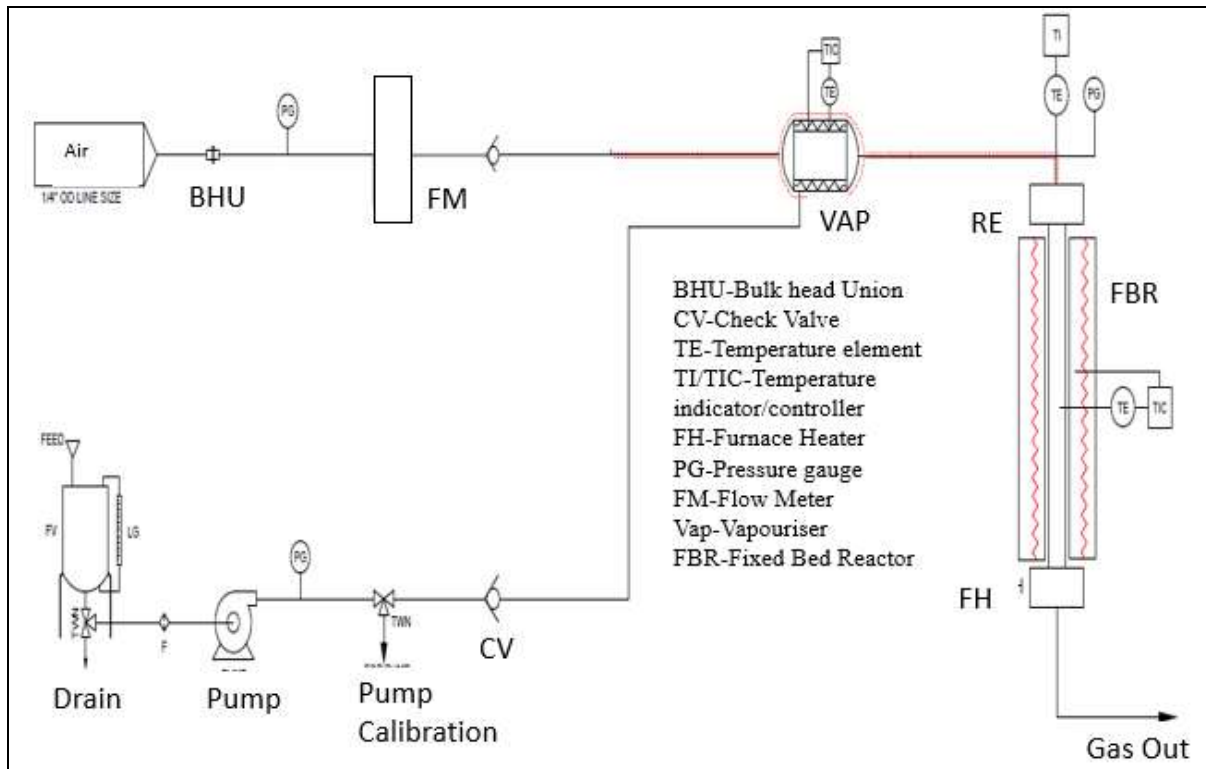
Fig.1. P & ID for a Fixed Bed Catalytic Reactor

Results and Discussion

Structural characteristics

The X-ray diffraction profile for PCN, PCN-CSG, PCF and PCF-CSG series are shown in **Fig.2.** The XRD profiles showed the presence of perovskite phase and the materials crystallised in orthorhombic symmetry. The S_{BET} values for $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) are shown in **Table 1**. For both the series there is a continuous increase in S_{BET} values, suggesting Ce-dopant prompts the increase of surface area. SEM images for the materials synthesized are shown in **Fig.3** and **Fig.4**. For samples synthesised by CP method, irregularly shaped, very large sized particles are visible. For samples synthesized by CSG method flake-like particles and porous solids are visible.

Table 1. BET Surface Area Values

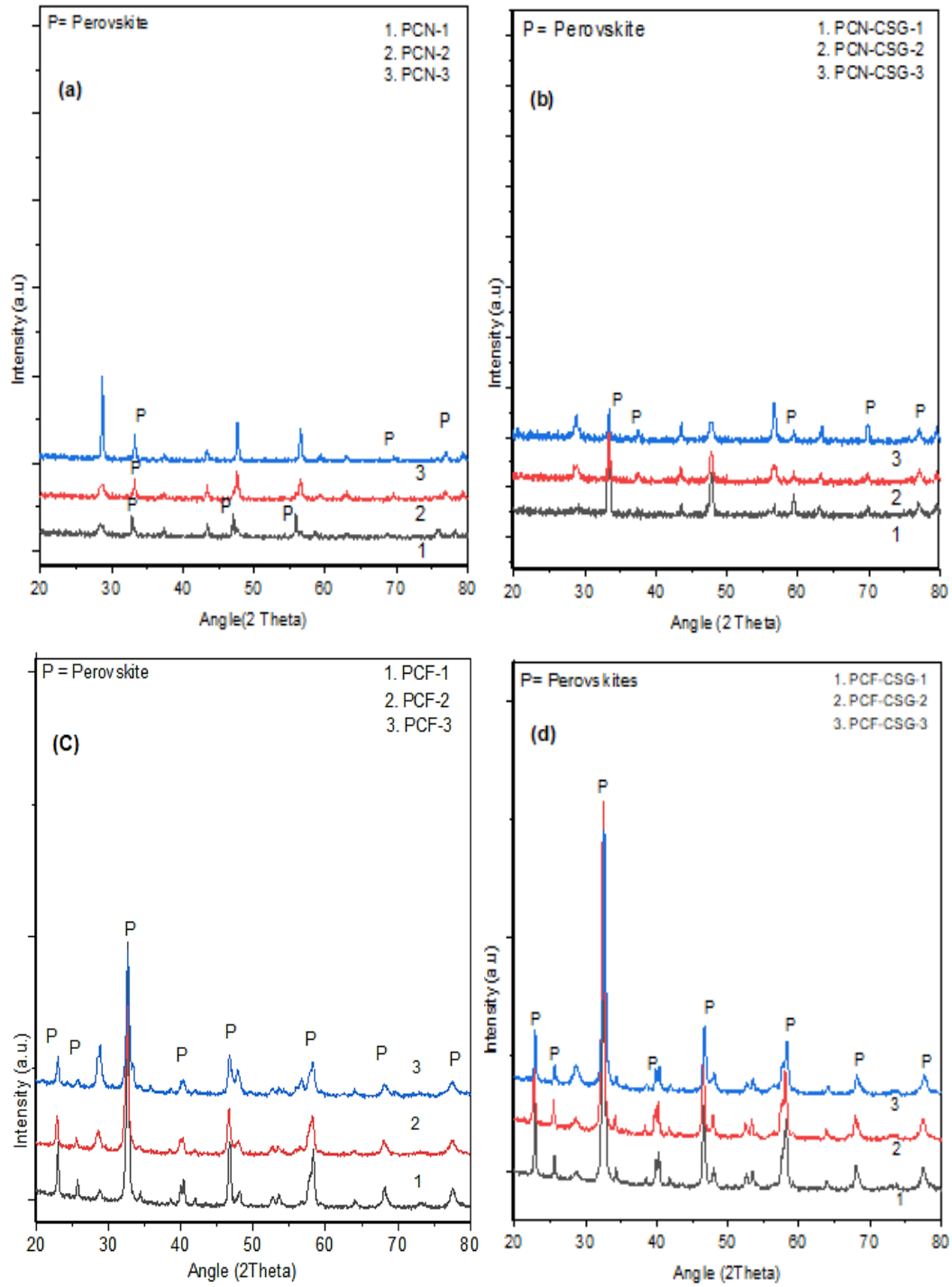| Materials	CP method		CSG Method	
	Code	S_{BET} (m^2/g)	Code	S_{BET} (m^2/g)
$Pr_{0.95}Ce_{0.05}NiO_3$	PCN-1	1.27	PCN-CSG-1	8.45
$Pr_{0.9}Ce_{0.1}NiO_3$	PCN-2	2.22	PCN-CSG-2	8.60
$Pr_{0.8}Ce_{0.2}NiO_3$	PCN-3	3.34	PCN-CSG-3	9.36
$Pr_{0.95}Ce_{0.05}FeO_3$	PCF-1	1.31	PCF-CSG-1	6.47
$Pr_{0.9}Ce_{0.1}FeO_3$	PCF-2	1.42	PCF-CSG-2	8.37
$Pr_{0.8}Ce_{0.2}FeO_3$	PCF-3	5.62	PCF-CSG-3	10.65

Fig.2. XRD patterns for (a) PCN (b) PCN-CSG (c) PCF and (d) PCF-CSG series

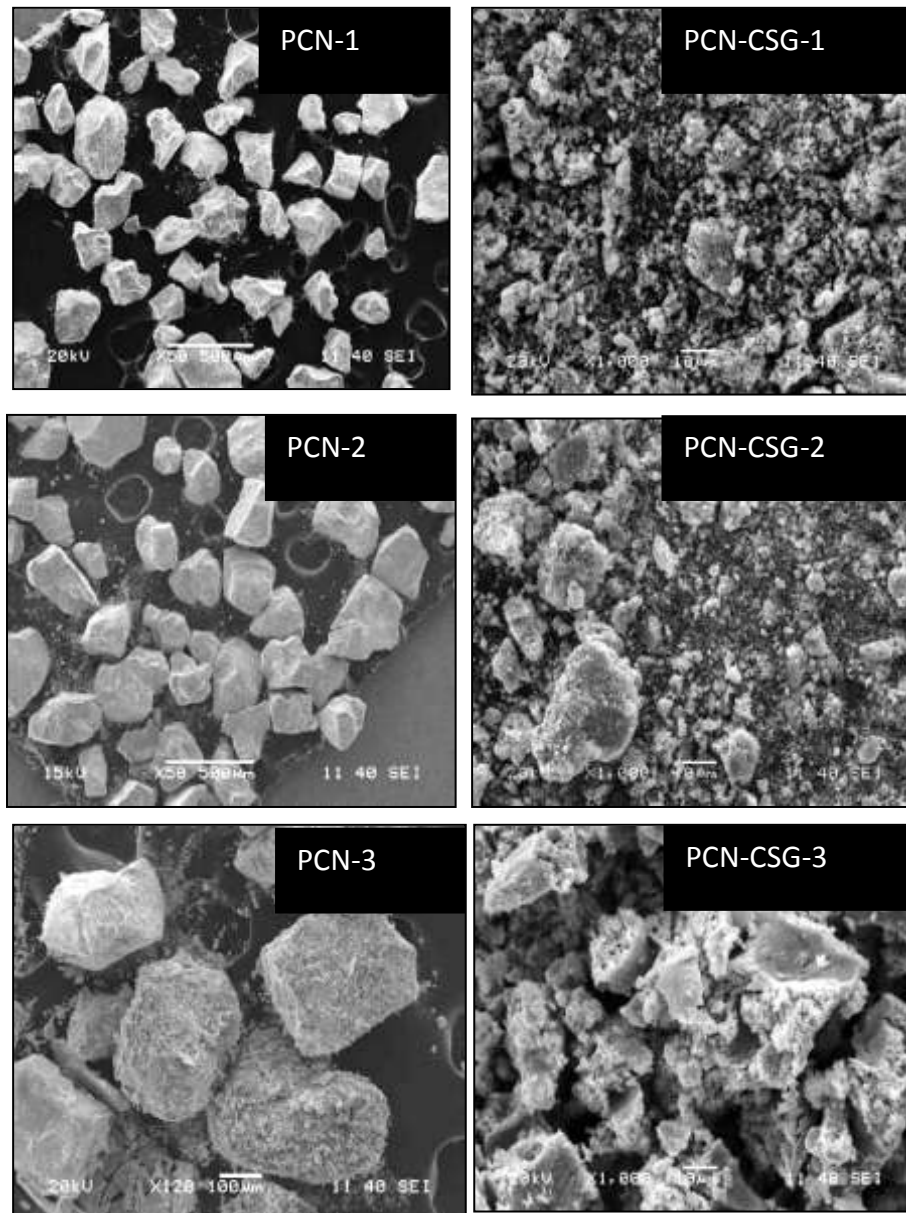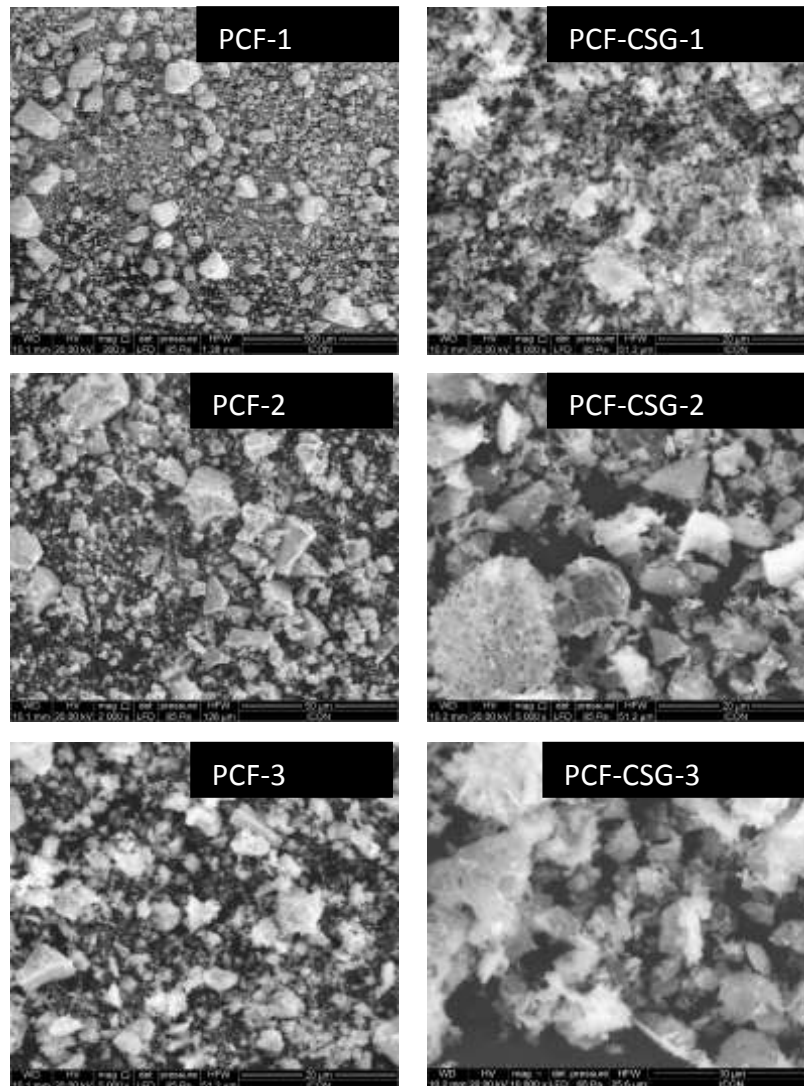**Fig.3 SEM Images for $Pr_{1-x}Ce_xNiO_3$**

Fig.4. SEM Images for $Pr_{1-x}Ce_xFeO_3$

The XRD profiles showed the presence of perovskite phase and the materials crystallised in orthorhombic symmetry (ICDD # 76-1004). Beyond, x = 0.1 amount of perovskite phase decreased and diffraction lines corresponding to CeO_2 became more intense. The thermodynamic stability of perovskites is limited by substitution of Pr by Ce. Since the ionic radii of Ce^{+4} and Ce^{+3} (0.097 nm and 0.114 nm) are close to Pr^{+4} and Pr^{+3} (0.096 nm and 0.113nm), there is a possibility to form Ce-substituted perovskites upon calcination. For $Pr_{1-x}Ce_xBO_3$ (B= Ni/ Fe) when x = 0.05 and 0.1, the major phase is a perovskite phase with some amount of ceria. However, for high Ce dopants (x>0.1) XRD patterns are dominated by peaks of ceria and weak peaks of nickel and iron oxides. Due to the possible amorphous nature of Pr_2O_3 phase or insertion of Pr^{+3} in CeO_2 structure, no detectable peak was observed for Pr_2O_3.

The increasing S_{BET} values with increasing value of 'x' may be related to the grain size of samples. The citrate sol-gel method resulted in a sponge-like product due to evolution of gases during the reaction of nitrate with organic component giving a voluminous and fluffy product with large surface area [24]. Additionally, formation of large amount of CeO_2 beyond x = 0.1, also contributed enormously to increased surface area of the samples.

The observations from SEM analysis are reliable with the estimated S_{BET} values, which demonstrate low S_{BET} values for materials prepared by CP method and high values for materials prepared via CSG technique. Particles tend to get clustered when prepared by CP method and this may well be the reason for low surface area of the materials formed. The observations from SEM analysis therefore indicates the effect of preparation methods on morphological characteristics of materials.

Catalytic activity determination

The synthesized perovskites were tested for DCE oxidation in a fixed bed reactor. The percentage conversions of DCE as a function of temperature (under steady state) is represented in **Fig.5**. The maximum temperature at which the reaction was analysed was 500°C. The T_{50} and T_{90} values that is the temperature for 50% and 90% conversion of DCE under the given reaction conditions are shown in **Table 2.** The T_{50} value for 50% conversion of DCE under the given reaction conditions lies in the range of 330°C to 500°C for $Pr_{1-x}Ce_xNiO_3$ series indicating lower catalytic ability of this series. Whereas, the T_{50} value for conversion of DCE for $Pr_{1-x}Ce_xFeO_3$ series is in the range of 320°C to 340°C. This indicates that 50% conversions are achieved at a relatively lower temperature. The T_{90} value for oxidation of DCE under the given reaction conditions was observed only for the catalyst PCF-CSG-3 at 490°C indicating excellent ability of this catalyst for DCE oxidation. The catalytic activity for undoped $PrNiO_3$ and $PrFeO_3$ for the oxidation of DCE was found to be low. On increasing the Ce-doping ratio,from 0.05 to 0.2, it was found that the catalytic activity for $Pr_{1-x}Ce_xNiO_3$ series increased for x = 0.05 and 0.1 and decreased for x = 0.2. For the $Pr_{1-x}Ce_xFeO_3$ the catalytic activity increased till x = 0.2. The catalytic activity was found to be low for materials synthesized via CP method as compared to materials synthesized by CSG method. The Ce-doping thus promotes an increase in the catalytic activity of the materials.
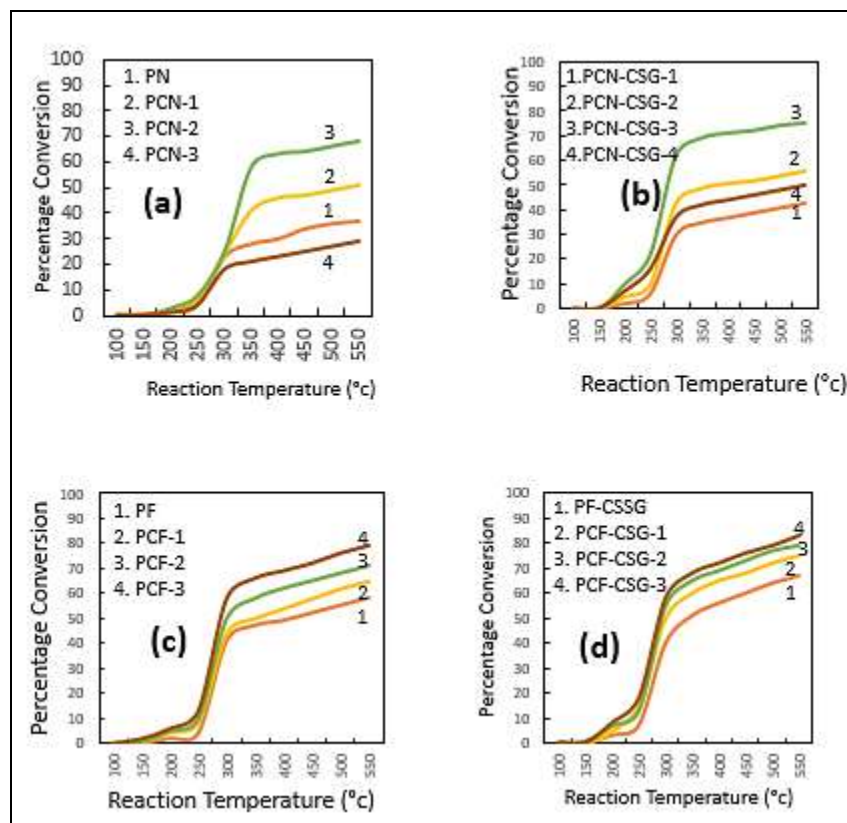

Fig.5 Catalytic Activity for oxidation of 1,2-Dichloroethane

Table 2 T_{50} and T_{90} values for DCE oxidation under given reaction conditions for $Pr_{1-x}Ce_xNiO_3$ and $Pr_{1-x}Ce_xFeO_3$

Catalyst (CP method)	T_{50} (°C)	T_{90} (°C)	Catalyst (CSG method)	T_{50} (°C)	T_{90} (°C)
PCN-1	495	-	PCN-CSG-1	475	-
PCN-2	345	-	PCN-CSG-2	335	-
PCN-3	-	-	PCN-CSG-3	500	-
PCF-1	340	-	PCF-CSG-1	335	-
PCF-2	333	-	PCF-CSG-2	330	-
PCF-3	328	-	PCF-CSG-3	321	490

Influence of increasing Ce substitution on physical properties of perovskites

In the XRD profiles, with x >0.1 the presence of ceria is detected along with scarce peaks of perovskites. Thus, in $PrNiO_3$ and $PrFeO_3$Ce can be partially substituted at A-site to form $Pr_{1-x}Ce_xNiO_3$ and $Pr_{1-x}Ce_xFeO_3$. Although the ionic radii for Pr^{+3} (0.113nm) and Ce^{+3} (0.114nm) are comparable, the diffraction pattern indicates that the thermodynamic stability of perovskite structure is limited by substitution of Pr by Ce. After doping ratio exceeds, x> 0.1, the materials turn out to be more of ceria- based structures and less of perovskites peaks are observed. The peaks also broaden with increasing Ce -doping ratio, which implies a decrease in particle size of the materials. With increasing Ce substitution, S_{BET} values go on increasing, the values being high for materials prepared by CSG method. The high S_{BET} values beyond, x > 0.1 indicates the contribution of CeO_2 phase to surface area of the materials. The SEM images does not show any significant morphological differences upon increase in Ce substitution in materials prepared via CP method. However, the CSG method gives flaky and porous materials with increasing Ce substitution as compared to the big sized particles obtained by CP method.

Catalytic activity of $Pr_{1-x}Ce_xBO_3$ for oxidation of 1,2-dichloroethane (DCE)

In case of Ce-doped series with x≤ 0.1 most of the Ce^{+4} ions are introduced into A-site for forming perovskites with presence of additional ceria. The presence of cerium in perovskites is expected to enhance the activity and this could be explained in terms of oxygen vacancies and presence of multiple oxidation states of B-site element. To maintain electroneutrality upon doping, replacement of Pr^{+3} by Ce^{+4} leads to formation of oxygen vacancies or an increase in oxidation state of B site ion or both. Oxygen vacancies and not interstitials are the pre-dominant defects in perovskite oxides[25,26]. To explain the mechanism of oxidation of VOCs on perovskites, Voorhoeve*et.al.*[27] introduced the concept of intrafacial and suprafacial reactions. In intrafacial reactions, the lattice oxygen of the oxide is involved in the reaction while, in the suprafacial reactions surface oxygen are the dominant oxygen species involved in the reactions. Suprafacial reaction occurs in the lower temperature range since the adsorption equilibrium of oxygen is thermodynamically favourable. The surface concentration of adsorbed oxygen decreases at high temperatures, however the lattice oxygen becomes more mobile and hence more available for the oxidation process. This results in transition of mechanism from suprafacial to intrafacial. The possible mechanism for oxidation of Cl-VOCs is shown in **Fig.6.**
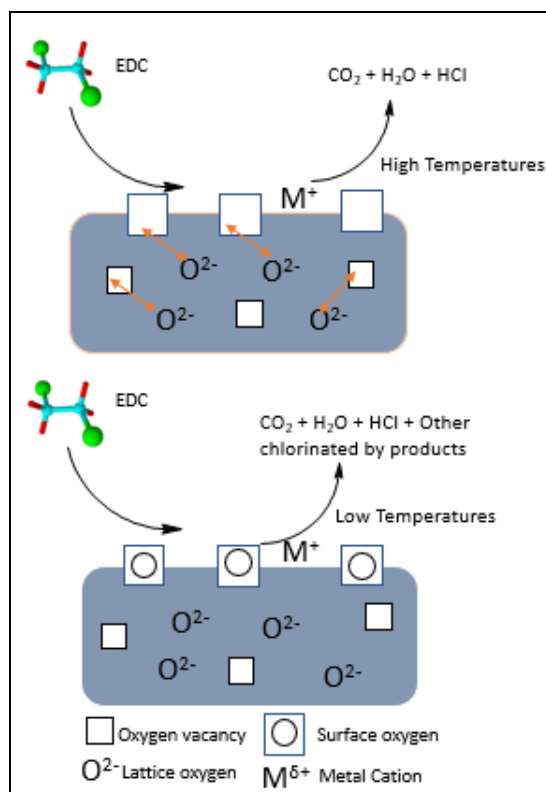

Fig.6 Possible mechanism for oxidation of Cl-VOCs on perovskites

In case of $Pr_{1-x}Ce_xNiO_3$, at high Ce content (x>0.1), the only Ni containing phase detected in XRD is NiO, which develops into large Ni^0 crystallites upon activation. This may well be the reason for the lowest catalytic activity of $Pr_{0.8}Ce_{0.2}NiO_3$ amongst the three catalysts. In case of $Pr_{1-x}Ce_xNiO_3$ (x = 0.05 and 0.1) perovskite structure is present in large amounts, providing well dispersed metals incorporated in the structure, due to which these catalysts show high catalytic activity. The presence of small amounts of ceria wherein, its excellent oxygen storage capacity may also influence the high catalytic activity of the catalysts for x = 0.05 and 0.1. Catalysts prepared by citrate sol gel method showed better activity as compared to those prepared by co-precipitation method. Improved surface area and large amount of porosity incorporated into the catalysts when prepared via sol-gel method could be the reason for their high activity.

In case of $Pr_{1-x}Ce_XFeO_3$, catalytic activity increases till x =0.2. The linear dependence of catalytic activity could be attributed to Mars-Van Krevelen redox cycle[28]. In this mechanism, the lattice oxygen migrates towards the surface and is consumed for the oxidation of adsorbed substrate and is quickly replenished by oxygen coming from the gaseous phase. The higher reaction rate could be attributed to an increase in the number of active sites. At low Ce-doping ratio x≤0.1, charge compensation might occur by oxidation of part of Fe^{+3} to Fe^{+4}. Hence, in $Pr_{1-x}Ce_XFeO_3$, Fe^{+3}/Fe^{+4} plays an important role and the active sites would be associated with Fe^{+4}. Higher the Ce-content, higher the number of active sites. Due to this condition, there occurs an increase in catalytic activity upon increase in Ce-doping ratio. This may be due to the that lattice oxygen is nearer to Fe^{+4} so that it can be reacted away with simultaneous reduction of Fe^{+4} to Fe^{+3}. Fresh oxygen can then be replenished on the generated oxygen vacancies, which then continues the cycle of redox reaction. It can thus be observed that T_{90} is detected for only a single catalyst (PCF-CSG-3) in the entire $Pr_{1-x}Ce_xBO_3$ series. The activity for $Pr_{1-x}Ce_XFeO_3$ can also be correlated to the BET surface area of these catalyst. As is evident from the data presented, that as the BET surface area of the catalyst increases, there is an increase in their catalytic activity. Catalyst prepared by sol-gel method showed improvements in perovskite formation with Ce well incorporated into the structure, surface area values and porous nature of the materials. All these improvements contributed to higher activity as compared to catalysts prepared by co-precipitation method.

By-product analysis of oxidation reaction using GC-MS

In $Pr_{1-x}Ce_xBO_3$perovskites, the dehydrochlorination of DCE to vinyl chloride occurs at high temperature (> 300°C). The nature of by-products in absence of water in the reactor feed has been evaluated using GC-MS technique. The main by-product is found to be vinyl chloride. Other by-products such as 1,2-dichloroethene, tetrachloroethane, trichloroethene, chloroform and carbon tetrachloride were formed in low concentration. **Fig.7** shows vinyl chloride (VC) selectivity as a function of temperature over representative catalysts from each series. It was observed that VC formation was higher at 400°C. Sinquin*et al*. have carried out catalytic oxidation of DCE on perovskites[6,29] in presence of water in the reactor feed. It was observed that in the presence of water, inhibition of polymerisation of VC occurs due to which the maxima for VC formation occurs in lower temperature range. Water prevents polymerisation of vinyl chloride by competing for Lewis acid sites and hence could be further oxidised before polymerisation occurs [29]. However, conversion of DCE at higher temperatures seems to be relatively unaffected by the presence of water in the feed and the activity is restored [6]. The fact that the present study was carried out in the absence of water maybe the reason for a high temperature maxima range for VC formation, suggesting polymerisation of VC in this temperature range. However, since dehydrochlorination at higher temperature range occurs without water impacting the reaction, these catalysts could be promoted as potential materials for oxidation of DCE. Further a decrease in reactor feed volume could also lead to enhancement in the catalytic activity.
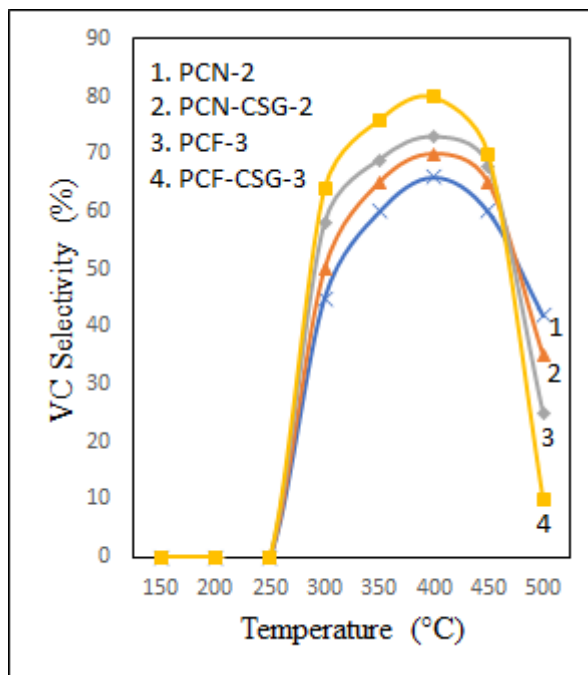
Fig.7 VC selectivity as a function of reaction temperature over representative catalysts

Stability study

Stability study was undertaken using the catalysts PCF-CSG-3, which according to the above discussion is an optimum catalyst. For determining the stability of the catalyst, three consecutive runs were performed using the PCF-CSG-3 catalyst in the fixed bed catalytic reactor. **Fig. 8** displays the corresponding curves for DCE oxidation for the three consecutive runs. No appreciable deactivation of catalyst was detected for the catalysts for the first two runs and the two curves overlapped each other. For the third run however, a slight deviation for catalytic activity was observed. This could be possibly due the 1% vol. feed of VOC concentration used in the oxidation studies. The T_{50} value remained unchanged for the first two runs, however it deviated slightly for the third run.
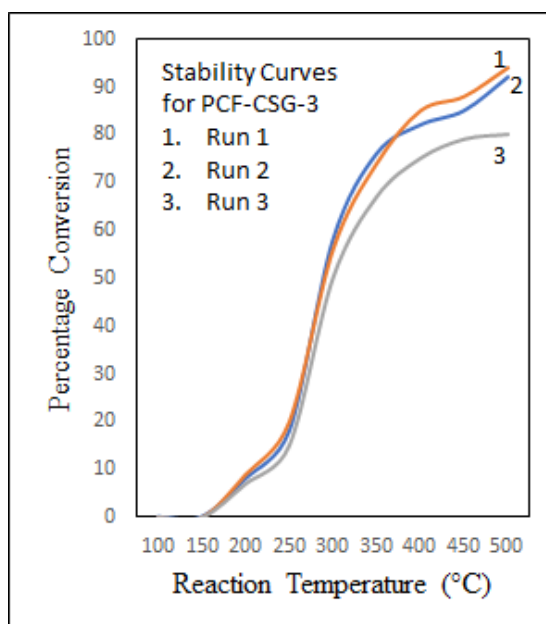

Fig. 8 Stability curves for PCF-CSG-3

Conclusion

The $Pr_{1-x}Ce_xBO_3$ (B= Ni/Fe) perovskite type oxides were synthesized by CP and CSG methods. XRD profiles revealed the presence of perovskite phase. However, beyond x = 0.1, the ceria phase became more dominant over the perovskite phase, indicating the thermodynamic limitations for doping Ce into $PrNiO_3$. The S_{BET} values increased on increasing Ce-doping, however, for materials with x = 0.2, the CeO_2 phase contributed enormously to the surface area. SEM images showed large particles for materials prepared with CP method while flaky, porous particles were obtained when materials were synthesised via CSG method. The catalytic activity for oxidation $Pr_{1-x}Ce_xBO_3$ increased till x = 0.1 and decreased thereafter. In case of $Pr_{1-x}Ce_xNiO_3$ high catalytic activity can be explained by taking into consideration, combined effects of perovskite structure present in large amounts, providing well dispersed Ni-metal and Ce incorporated in the structure. It may be suggested that in $Pr_{1-x}Ce_xNiO_3$ for x > 0.1, due to the segregation of NiO, the catalytic activity decreases due to the loss of oxygen vacancies. In case of $Pr_{1-x}Ce_xFeO_3$, presence of iron ions in unusual oxidation states (+4) and oxygen vacancies were responsible for the high catalytic activity. The catalytic activity for $Pr_{0.8}Ce_{0.2}FeO_3$ was found to be highest. The results also prove that CSG method is advantageous in a way leading to formation of well crystallised perovskite phase, improved surface area and highly porous materials, which in turn also leads to an increase in their catalytic activity for oxidation of DCE. In perovskites presence of oxygen vacancies and variation of oxidation states of transition metals producing lattice defects are most likely to contribute to high catalytic activity[30], which modifies the oxygen adsorption-desorption properties. With enhancement in reactor parameters, the VOC feed could be reduced to 0.1% vol, which may lead to a further increase the catalytic activity of the synthesized materials. The conversion of DCE at higher temperatures seems to be relatively unaffected by the presence of water in the feed. Vinyl chloride was found to be the major by-product of the oxidation reaction. PCF-CSG-3 was found to be the optimum catalyst and it was found to be stable for two consecutive reaction runs at a VOC concentration of 1% vol. However, further research seeks to perform the reaction in presence of 4- 5% vol. of water. Thus, these materials could prove as potential catalysts for the oxidation of DCE and other VOCs of industrial concern.

Acknowledgement

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