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PAPER

Improving Catalytic Activity of PrMO_3 (M= Co and Fe) Perovskites: Synthesis of Thermally Stable Nano-particles by a Novel Hydrothermal Method

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A novel and simple hydrothermal synthesis method using metal cyano complex precursors was demonstrated to synthesize nano-sized PrCoO_3 and PrFeO_3 perovskites. It was possible to achieve significantly improved catalytic properties, but more importantly with thermal stability and purity of perovskite phases in their nanoparticle form. These materials were characterized by means of X-ray powder diffraction, FE-SEM, HR-TEM as well as H_2 -TPR analysis, and evaluated for their catalytic activity towards CO oxidation reaction. Both the nano perovskites were able to retain their morphology achieved through hydrothermal treatment, even after high temperature calcination. The catalytic activity of these materials was also compared with conventionally synthesised materials using solid state method, as well as those reported in literature. The superior catalytic activity of PrCoO_3 catalyst for CO oxidation over PrFeO_3 catalyst is mainly because of better redox properties and may also be due to preferential adsorption of CO on PrCoO_3 perovskite at low temperature. However, the marked improvement in catalytic activity for both nano perovskites was primarily due to their improved surface area and better reducibility, which can be attributed to their nano form. It appears possible to control the particle size as well as shape of perovskites using this improved synthesis method, while more importantly, it was possible to reduce sintering and agglomeration of perovskites. While the method has potential to apply for synthesis of several other mixed oxides materials in nano form, it will be important to investigate other physical properties of such thermally stable nano perovskites.

INTRODUCTION

²⁵ Since last few decades, perovskite type compounds have been considered as potential materials for their properties related to high temperature superconductivity, magnetoresistance, ionic conductivity, dielectric properties, sensors, solid-oxide fuel cell (SOFC), membrane separation, catalysis and many other applications.¹⁻⁷ Especially in catalysis, perovskites are well explored materials for CO, hydrocarbon oxidation as well as de- NO_x reactions, and considered as potential substitutes for noble metal based three-way and soot oxidation catalysts. The general chemical formula of perovskite is ABO_3 , in which, A ions can be rare earth, alkaline earth and other large ions, while B ions are generally first row transition metal ions. In this ABO_3 structure, often the A cation has twelve fold coordination with oxygen, while the coordination number for B cation is 6.⁸⁻¹¹ Perovskites are usually prepared by high temperature calcination method, which results in sintered and agglomerated phases (large particle size) with low surface area. This is a major limitation in spite of their tailored properties and high intrinsic catalytic activity. Many research works have been therefore, reported on improved low temperature synthesis of perovskites, including co-precipitation,

⁴⁵ solution combustion, sol-gel and surfactant based synthesis methods to achieve higher surface area, as well as nano structures.¹²⁻¹⁸ However, low temperature synthesis often leads to undesired impurity phases and poor crystallinity, thereby leading to loss of catalytic activity, thus making the scientific interpretations difficult. Many of these perovskites synthesized at lower temperatures, also lose their surface area and other properties, once subjected to higher temperature exposures, due to agglomeration or sintering. Such materials therefore, cannot be used for high temperature applications. In this way, synthesis of high purity, crystalline perovskite in smaller and nanoparticle form with higher surface area and thermal stability, is one of the important research areas of interest. This is especially important considering the fact, that properties of perovskites are often a function of their synthesis method. The main aim of present research work is to synthesize pure, crystalline and thermally stable perovskite nanoparticles by a novel hydrothermal method, using metal cyano complex precursors, explored for the first time to synthesize perovskites as per best of our knowledge.

There are research works reported on perovskite synthesis by using several routes, including thermal decomposition of metal cyano complex. Gallagher reported the synthesis of perovskite by

thermal decomposition using metal cyano coordination complex.¹⁹ Sadaoka et al. extensively studied the thermal decomposition of metal cyano complex for perovskite synthesis, and reported different types of simple as well as tri-metallic rare earth based perovskites.²⁰⁻²² They also reported sensor and catalytic applications for perovskites, prepared by thermal decomposition of metal cyano complex.²³⁻²⁵ Recently, Asamoto et al. reported perovskite catalysts synthesized by thermal decomposition of metal cyano complex.²⁶ However, sintering/agglomeration of particles is still a challenge for perovskite synthesis, due to the requirement of high temperature calcination to obtain relatively pure phase. The present study is a successful attempt to overcome this problem, by applying a novel hydrothermal treatment to obtain nano sized perovskites by using metal cyano coordination complex as a precursor, prepared during the synthesis. The materials thus synthesized were subjected to physicochemical characterization by using XRD, FE-SEM, HR-TEM, BET-SA and H₂-TPR, techniques to understand their properties, and specially any change in these properties as a function of their nano form.

The catalytic activity for CO oxidation on thus synthesized perovskite materials was also studied using high CO concentration and high space velocity conditions. There are different catalysts reported for catalytic CO oxidation reaction, and the activity of present nano perovskite catalysts is quite comparable to those reported potential perovskite type catalysts. Asamoto et al. studied CO oxidation on SmCoO₃ and SmFe_xCo_{1-x}O₃ catalysts, prepared by thermal decomposition of cyano complexes. They reported T₅₀ at above 200 °C for SmCoO₃ for CO oxidation.²⁶ LaCoO₃ perovskite was synthesized by citrate method and studied for CO oxidation by Colonna et al. They reported complete CO conversion at around 230 °C on LaCoO₃.²⁷ Li et al. studied the synthesis of hierarchical LaFeO₃ fibers and compared the CO oxidation activity with LaFeO₃ particles prepared by conventional sol-gel method. They reported T₅₀ at 264 °C for LaFeO₃ fibers and 383 °C for LaFeO₃ particles.²⁸ Sun et al. studied CO oxidation on LaCoO₃ catalyst prepared by sol-gel method, and reported T₅₀ at 205 °C.²⁹ A series of Fe based lanthanide (La, Nd and Sm) perovskites synthesized using citrate method were systematically studied for CO oxidation by Ciambelli et al. They reported T₅₀ for SmFeO₃, NdFeO₃ and LaFeO₃ at 366, 321 and 348 °C respectively.³⁰ The present results (shown in Figure 5 and Table 2) on perovskite compositions confirm the improved catalytic properties of these non-noble metal based catalyst compositions, synthesized in nano, shape-controlled form. Noticeably, these particles are thermally stable and offer stable catalytic activity even with the synthesis temperature of more than 800 °C as well as on prolong exposure to CO containing gas mixture.

EXPERIMENTAL

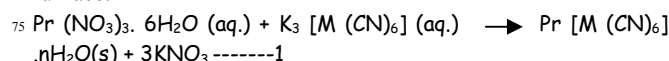
Materials

Laboratory grade praseodymium nitrate (Acros-India Ltd.), potassium hexacyanocobaltate (Sigma Aldrich), potassium hexacyanoferrate (Sigma Aldrich), cobalt oxide (Qualigenes), iron oxide (Merck) and praseodymium oxide (HIMEIA) were used directly without further purification.

Catalyst preparation

Hydrothermal synthesis using cyano complex precursor

Two PrMO₃ (M=Co and Fe) type catalysts were prepared by following a cyano-complex assisted hydrothermal synthesis method, and represented as PrCoO₃-CC and PrFeO₃-CC. 100 ml of hexacyano metal complex (0.005 moles) aqueous solution and 100 ml of praseodymium nitrate (0.005 moles) aqueous solution were prepared, and mixed by vigorous stirring. The resultant mixed metal complex (as given in equation 1) was hydrothermally treated using stainless steel Parr autoclave vessel, placed in an oven at 150-160 °C for 3 h. After hydrothermal treatment, the resultant complex was cooled to room temperature and separated by using a suction filtration. The complex/precipitate thus obtained was washed with distilled water, followed by methanol, and dried at 80 °C for 4 h in a laboratory oven. Finally, the solid mass was homogenized by grinding and subjected to calcination at 800 °C for 8 h in a muffle furnace.



(Where, M=Co or Fe; light green complex was obtained for Co, while brown precipitate complex was observed for Fe based precursor).

Solid state synthesis

PrMO₃ (M=Co and Fe) catalysts were also prepared by following conventional solid state route for comparison of their properties with nano-perovskites, and the synthesised materials were denoted as PrCoO₃-SS and PrFeO₃-SS, respectively. PrCoO₃-SS was synthesized by thoroughly mixing equimolar amounts of praseodymium oxide and cobalt oxide by physical grinding using a laboratory mortar and pestle. The mixture thus obtained was calcined at 1100 °C for 8 h in a muffle furnace. The above procedure was also used to synthesize PrFeO₃-SS catalyst using praseodymium oxide and iron oxide precursors.

Catalyst characterization

All the synthesized catalysts have been characterized by powder X-ray diffraction (XRD) technique using Ultima Rigaku machine (RINT2200) operated at 40 kV and 40 mA with a monochromator using Cu- α radiations. The specific surface area of samples was analysed by following standard nitrogen adsorption method using QuadraSorb SI, Quantachrome instrument. The morphological and structural information of the materials were studied by field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM) analysis. FE-SEM investigations were carried out using JEOL (JSM-6340F) instrument. The HR transmission electron microscopic studies were carried out by using a JEOL JEM-3010 microscope, operated at 300 kV (LaB₆ cathode, point resolution 1.7 Å), to study the morphology as well as structural details of the perovskites. The sample was dispersed in ethanol and treated in ultrasound device for 10 minutes. A drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at ambient temperature.

Temperature programmed reduction (H₂-TPR) analysis were performed using a BEL-CAT, BEL Japan instrument, equipped with a TCD detector. A fixed bed of granules of catalyst was placed in a quartz tube and prior to each of H₂-TPR experiment, the catalyst was pretreated under a flow of helium (30 ml/min) at 400 °C for 30 min and cooled to 40 °C under the same flow. The

reduction of catalyst was followed by heating the catalyst up to 800 °C at constant heating rate of 10 °C/min under the 5 % H₂-N₂ flow, and consumption of H₂ during the sample reduction step was determined by using a precalibrated TCD detector.

5 Catalytic activity measurements

The catalytic CO oxidation was studied using a fixed bed, steady state type catalyst evaluation reactor. Granules of catalysts (0.1 g) were packed in a quartz reactor for catalytic run, and temperature of the reactor was maintained by using PID controlled furnace.

10 Prior to the catalytic activity test, the catalysts were pretreated at 400 °C for 30 min in flow of helium for surface cleaning. The total flow rate of 50 SCCM of high purity gases (0.5% CO balance He and 5% O₂; W/F=0.12 g s/ml) were measured by mass flow controllers (HORIBA, Japan). After the catalyst had
15 attained steady state over a period of 30 min at each temperature, the effluent gas was analysed for CO and CO₂ by a gas-chromatograph (Shimadzu) using a Molecular Sieve 5A as well as Porapak columns.

RESULTS AND DISCUSSION

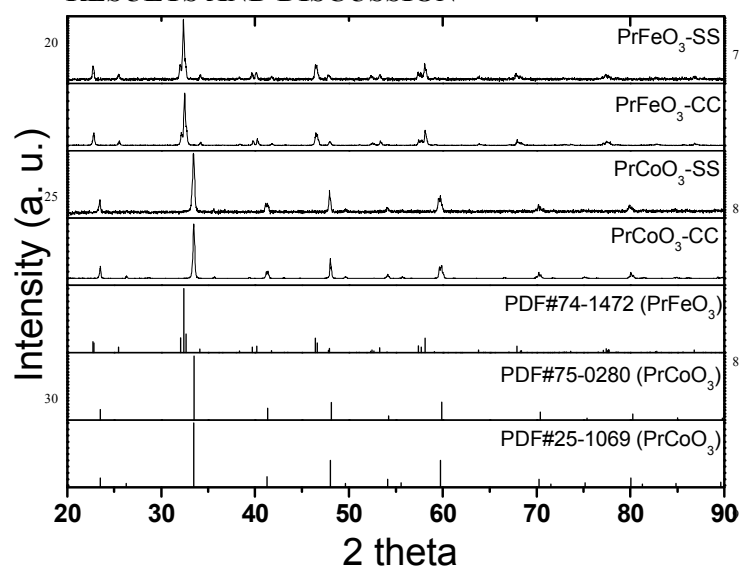


Fig. 1: XRD patterns of catalysts

The X-ray diffraction analysis (Fig. 1) clearly inferred that the synthesized materials possess crystalline and single phase perovskite structure. The PrCoO₃-CC belongs to cubic system, while orthorhombic crystalline structure was observed for
40 PrFeO₃-CC sample, which was confirmed by referring to Joint Committee on Powder Diffraction Standards (JCPDS- 25-1069, 75-0280 and 74-1472, respectively) database. X-ray diffraction analysis for both solid state route prepared samples PrCoO₃-SS and PrFeO₃-SS was also performed. As depicted in Fig.1, these
45 X-ray diffraction patterns clearly revealed the formation of perovskite phases in these samples as well. X-ray diffraction analysis, however, suggests that these solid state route catalysts possess inferior crystallinity than cyano complex based hydrothermally synthesized perovskites, though the calcination
50 temperature used for the former samples was much higher than those synthesized by improved cyano-complex method. Thus the present cyano-complex method provides adequate conditions for metal ions to form a precursor, while the hydrothermal treatment

leads to crystallization of perovskite phase at milder temperature. Once nano-particles are formed, they are stable against the high temperature sintering.

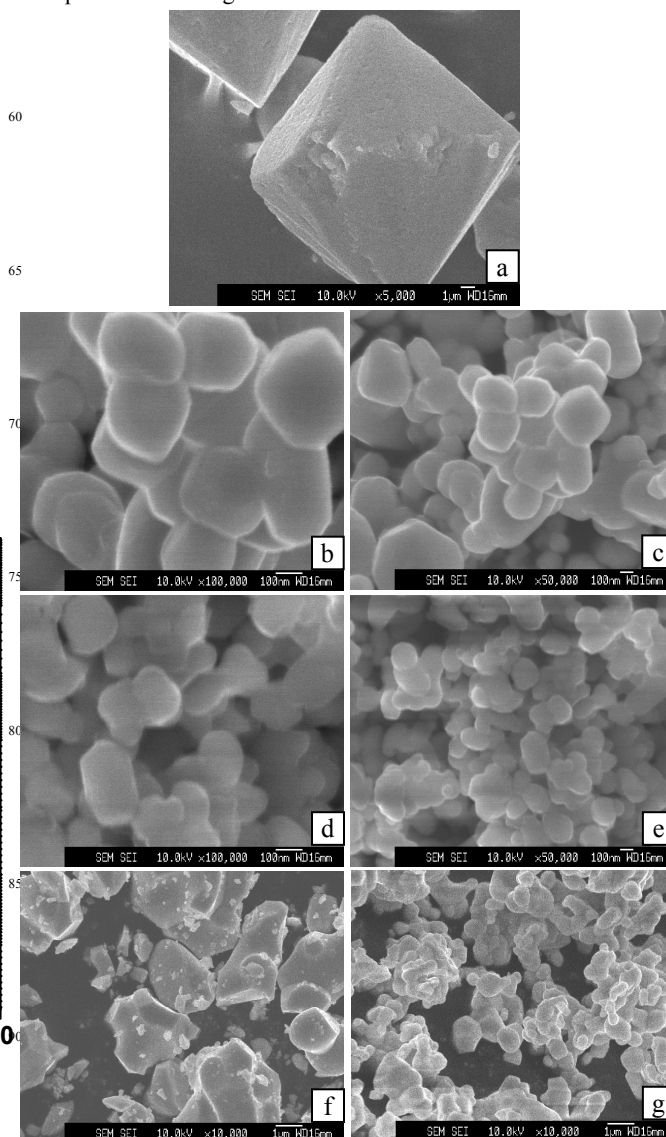


Fig. 2: a- FE-SEM image of Pr [Co (CN)₆] complex precursor after hydrothermal treatment; b and c- FE-SEM image of PrCoO₃-CC; d and e- FE-SEM image of PrFeO₃-CC; f- FE-SEM image PrCoO₃-SS; g- FE-SEM image of PrFeO₃-SS

The particle size, shape and other morphological details of the perovskite materials were studied by FE-SEM and HR-TEM analysis. As depicted in images (Fig. 2 and 3), the size as well as shape of perovskite particles could be controlled after optimization of process, which is mainly because of the use of cyano complexes and the hydrothermal treatment. These synthesis steps lead to controlled nucleation and growth of crystallites, thereby offering much controlled synthesis of
100 perovskite precursors. FE-SEM images (Figs. 2 (a-e)) show morphology of Pr[Co(CN)₆] complex precursor after hydrothermal treatment (a), PrCoO₃-CC (b-c) and PrFeO₃-CC (d-e) with different magnification. Figs. 2 (f and g) clearly suggest the formation of agglomerates of perovskite particles in case of
105 catalysts prepared by solid state route. The particle growth of

several microns is clearly visible for PrCoO₃-SS, while some small particles seen are the broken particles during grinding as also indicated by their irregular shapes. Relatively regular shaped particles were observed in case of PrFeO₃-SS, however, most of these particles are of the order of one micron and larger. Fig. 3(a-c) and (d-f) show the HR-TEM images of PrCoO₃-CC and PrFeO₃-CC respectively. TEM images of both the samples inferred practically no agglomeration of particles, which would be usually expected for conventionally synthesized mixed oxide materials with high temperature calcination.¹⁶ Although, SEM images for PrFeO₃-CC do shows some particles above 100 nanometres, the particle size is much smaller than those synthesized by solid state route.

The SEM (Fig. 2 (a-e)) and TEM analysis therefore, clearly inferred that the synthesized perovskite particles are of nano size without agglomeration. Particle size of about 100 nm with cubic structure was observed for PrCoO₃-CC, while for PrFeO₃-CC, particle size of <100 nm with hexagonal morphology was determined. TEM images (Fig. 3-c and 3-e) also confirm the formation of rather ordered morphology for both PrCoO₃-CC and PrFeO₃-CC perovskite samples. As mentioned, the particle size control was not only because of metal cyano coordination complex precursor offering the desired proximity and homogeneity of precursor metal ions, it was also because of the hydrothermal treatment of precursor solution offering better conditions for nucleation and crystallization of perovskite structures. As shown in Table 1, BET-surface area results of cyano-complex based perovskites are much better than conventionally prepared catalysts. The lower surface area of solid-state synthesized catalysts is mainly because of high temperature calcination, which leads to sintering, as seen in FE-SEM images (Fig. 2 (f and g)) as well.

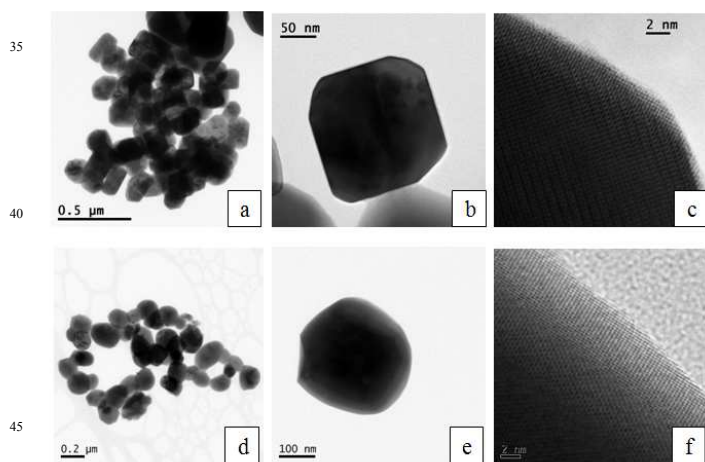


Fig. 3: a-c-HR-TEM images of PrCoO₃-CC; d-f- HR-TEM images of PrFeO₃-CC

Table 1: BET-SA of catalysts

| Catalyst | S _{BET} (m ² /g) |
|------------------------|--------------------------------------|
| PrCoO ₃ -CC | 10.1±0.5 |
| PrCoO ₃ -SS | 2.7±0.1 |
| PrFeO ₃ -CC | 6.1±0.3 |
| PrFeO ₃ -SS | 3.1±0.2 |

The hydrogen temperature programmed reduction (H₂-TPR) studies were carried out to understand the oxygen non-stoichiometry and redox properties of these catalysts.

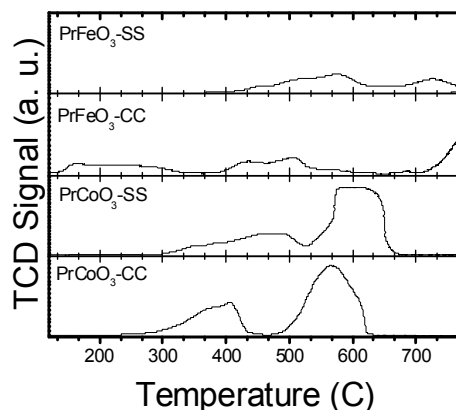


Fig. 4: TPR profiles of catalysts

The H₂-TPR profiles for all the samples are depicted in Fig. 4. Well distinguished, quite high intensity reduction peaks were observed for PrCoO₃ catalysts as shown in TPR profile. The first low temperature peak should correspond to the reduction of Co³⁺ to Co²⁺, while the second reduction peak at higher temperature should be due to the reduction of Co²⁺ to metallic cobalt.^{29, 31-32} For PrCoO₃-CC catalyst, the Co³⁺ to Co²⁺ reduction peak was observed at ≈ 250-430 °C, while this reduction was significantly shifted towards higher temperature (≈ 300-530 °C) for PrCoO₃-SS catalyst. Second high temperature Co²⁺ to metallic Co reduction was observed at ≈ 465-625 °C for PrCoO₃-CC catalyst, while this reduction peak was also observed at much higher temperature of ≈ 530-670 °C for PrCoO₃-SS catalyst. This reduction behaviour is clearly due to the smaller particle size of PrCoO₃-CC, which inferred the better reducibility of same composition in the nanoparticle form.³²⁻³⁵ In case of PrFeO₃ catalysts, the observed reduction was relatively very low.³⁶⁻⁴⁰ At lower temperature (≈ 160-640 °C), quite small peak for hydrogen consumption was observed, which could be due to the reduction of Fe⁴⁺ to Fe³⁺ along with Fe³⁺ to Fe²⁺ on catalyst surface sites, as also reported by other researchers.^{30, 41-44} This low temperature reduction was observed at ≈ 160-600 °C for PrFeO₃-CC, while this reduction peak was observed relatively at higher temperature (≈ 420-640 °C) for PrFeO₃-SS catalyst. In case of PrFeO₃-CC catalyst, a sharp reduction peak was observed at high temperature (above 700 °C), which should correspond to the reduction of Fe³⁺ to Fe²⁺ in bulk.⁴⁵ For PrFeO₃-SS catalyst, however, at 700 °C no significant reduction of Fe³⁺ to Fe²⁺ was observed. Hence, it is very clear from the TPR results, that the improved redox properties of perovskites prepared by hydrothermal synthesis

using cyano complex route is mainly because of their nano form. For both PrCoO₃-CC and PrFeO₃-CC samples, practically no significant sintering was observed at 800 °C, which could be the main factor to achieve improved redox properties. In this way, it is possible to improve the redox properties of perovskite materials by synthesizing them in nanoparticle form even using high temperature synthesis temperature, which makes them suitable for high temperature catalytic applications.

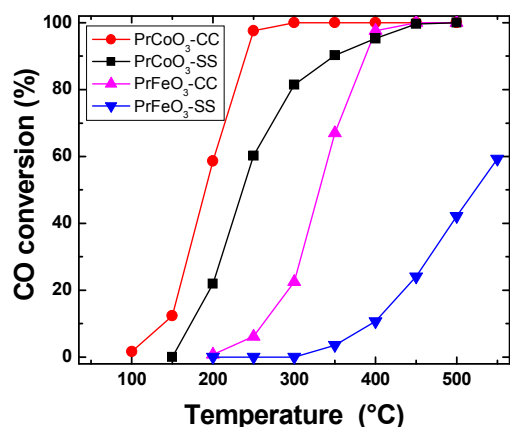


Fig. 5 CO oxidation as a function of temperature (Feed: 0.5% CO + 5% O₂; space velocity $\approx 50,000$ h⁻¹)

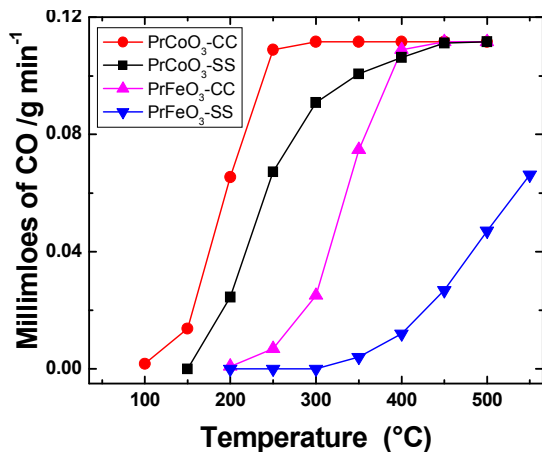


Fig. 6 TOF as a function of temperature (Feed: 0.5% CO + 5% O₂; space velocity $\approx 50,000$ h⁻¹)

The catalytic activity results of all the catalysts for CO oxidation are presented in Fig. 5, and the comparative results of T₅₀, T₉₀ and TOF values are given in Table 2. The light-off temperature for PrCoO₃-SS was observed around 150 °C, while T₉₀ at 350 °C. Much improved CO oxidation activity was observed for PrCoO₃-CC sample. The CO oxidation starts at temperature below 100 °C, and reaches T₉₀ at around 235 °C. In case of PrFeO₃-SS, the reaction starts around 300 °C and barely about 60 % CO conversion was achieved at 550 °C, whereas remarkably improved CO oxidation activity was observed for PrFeO₃-CC catalyst. The CO oxidation reaction begins at 200 °C, and reaches T₉₀ at around 383 °C. These results clearly inferred the much improved catalytic performance for perovskite samples prepared

by cyano complex based hydrothermal method. Relatively, much better activity was observed for both the cobaltate based perovskites as compared to PrFeO₃ samples, especially at temperature below 250 °C. This is obvious due to the presence of cobalt, which is very active for CO oxidation reaction. Fig. 6 shows the TOF (Turn over frequency) for the CO oxidation reaction. TOF was calculated as millimoles CO converted per gram of catalyst per unit time. Maximum 0.1089 mmol CO conversion per gram of catalyst was observed, when PrCoO₃-CC perovskite oxide shows 98% conversion at 250 °C, whereas PrCoO₃-SS catalyst converts a maximum of 0.06723 mmol of CO at the same temperature. For PrFeO₃-CC catalysts, maximum of 0.00684 mmol of CO conversion per gram was obtained at 250 °C, while the TOF was negligible for PrFeO₃-SS at the same temperature. The activity in terms of millimoles of CO oxidized per unit mass of PrCoO₃-CC and PrCoO₃-SS was about sixteen and ten times respectively higher than that observed for PrFeO₃-CC at temperature of 250 °C. This higher catalytic activity is because of better redox properties of PrCoO₃ as corroborated with H₂-TPR results, and also due to preferred adsorption of CO on PrCoO₃ cobaltate at lower temperature. However, the more striking finding is the relatively much improved catalytic activity for the cyano complex based nano-catalysts as compared to those prepared by conventional synthesis, with the same compositions. As evidenced from Table 2, much improved T₅₀ and T₉₀ values were observed for both these nano perovskite samples prepared by cyano complex method, as compared to those prepared by using conventional solid state method. Considering their nano form, stability of both PrCoO₃-CC and PrFeO₃-CC nano perovskite catalysts was examined after CO oxidation reaction, by means of XRD and H₂-TPR analysis. There is no change observed in structure as well as redox properties of both the catalysts even after 30 h exposure to reaction mixture of 0.5% CO along with 5% O₂. Both the catalysts show practically unchanged catalytic activity after the CO exposure experiment.

Table 2: Comparative T₅₀, T₉₀ (°C) and TOF results

| Catalysts | T ₅₀ (°C) | T ₉₀ (°C) | TOF at 250 °C |
|------------------------|----------------------|----------------------|---------------|
| PrCoO ₃ -CC | 190 | 235 | 0.10892 |
| PrCoO ₃ -SS | 235 | 350 | 0.06723 |
| PrFeO ₃ -CC | 332 | 383 | 0.00684 |
| PrFeO ₃ -SS | 523 | - | - |

Table 3: Pseudo first-order rate constant per specific surface area (k_s) and activation energy (Ea) for CO oxidation on perovskite catalysts (^{a,b} k_s at 200 °C; ^{c,d} k_s at 400 °C)

| Catalyst | S _{BET} / m ² g ⁻¹ | k_s / mmol s ⁻¹ m ⁻² | Ea / KJ mol ⁻¹ |
|-------------------------------------|---|--|---------------------------|
| PrCoO ₃ -CC ^a | 10.1±0.5 | 0.0325 | 50.3 |
| PrCoO ₃ -SS ^b | 2.7±0.1 | 0.0341 | 58.6 |
| PrFeO ₃ -CC ^c | 6.1±0.3 | 0.2275 | 84.6 |
| PrFeO ₃ -SS ^d | 3.1±0.2 | 0.0136 | 80.8 |

In order to understand the impact of specific surface area (S_{BET}) on catalytic activity, the rate constant per S_{BET} was also

calculated by assuming the pseudo first-order reaction to CO concentration. As shown in Table 3 and Fig. 7a, catalytic activity per unit S_{BET} for CO oxidation for $\text{PrCoO}_3\text{-CC}$ and $\text{PrCoO}_3\text{-SS}$ is rather similar, despite significant difference in their T_{50} and T_{90} temperatures. Therefore, the similar catalytic activity for these catalysts after normalization with their specific surface area, clearly inferred that the improved surface area in case of $\text{PrCoO}_3\text{-CC}$ is mainly responsible for its improved catalytic activity. Although marked improvement in catalytic activity was observed for $\text{PrFeO}_3\text{-CC}$ sample as compared to $\text{PrFeO}_3\text{-SS}$, however, Fig. 7b suggests that this improvement is not solely due to the improved surface area. As the intrinsic activity for $\text{PrFeO}_3\text{-SS}$ catalyst was quite low, its synthesis in nano form appears to improve its reducibility (as evidenced with TPR results) and thus its intrinsic catalytic activity, in addition to its physical properties like surface area. As depicted in Table 3 for CO oxidation reaction, the activation energy (E_a) value of PrCoO_3 is lower than of PrFeO_3 . The lower E_a of PrCoO_3 could be related to the better redox property of Co based perovskites. Effect of space velocity on catalytic activity was also studied using different feed flow rate and keeping the catalyst amount constant. No adverse effect on CO conversion was observed and the catalyst shows excellent CO oxidation even at high space velocity conditions. In this way, these two perovskite type compositions, PrCoO_3 and PrFeO_3 show significant improvement in their catalytic activity achieved through their synthesis in nano form, using present cyano complex based hydrothermal method. The enhanced catalytic activity is primarily due to the enhanced surface area as well as redox properties as evidenced from the present study.

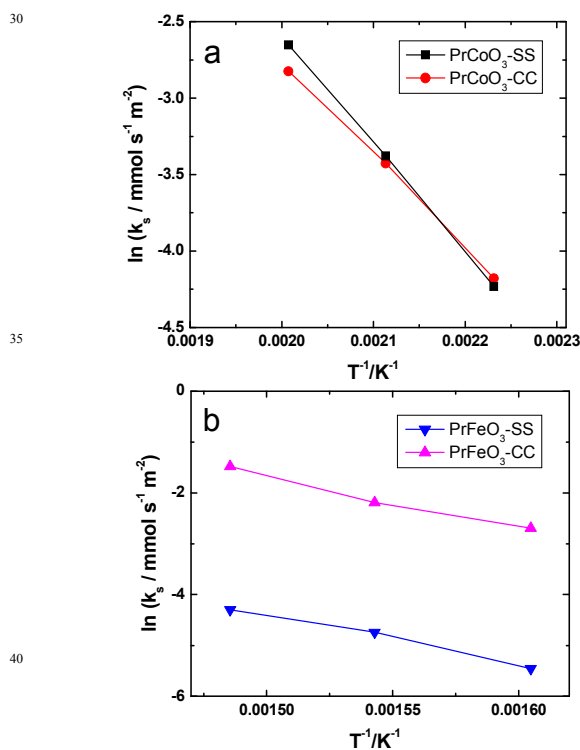


Fig. 7: Arrhenius plot for CO oxidation a- $\text{PrCoO}_3\text{-CC}$ and $\text{PrCoO}_3\text{-SS}$; b- $\text{PrFeO}_3\text{-CC}$ and $\text{PrFeO}_3\text{-SS}$ catalysts (Feed: 0.5% CO+5% O_2 balance He; SV \approx 50,000 h^{-1})

CONCLUSION

Nanoparticles of PrCoO_3 and PrFeO_3 compositions with perovskite type structure were successfully synthesized by following a simple hydrothermal method, using metal cyano complex as precursors. XRD and electron microscopic results confirm the formation of pure perovskite nano-crystallites of about 100 nm size, with regular morphology and without much sintering, despite calcination at higher temperature. In this way, the particle size and other physical properties of perovskite can be controlled even with high temperature calcination, by following present hydrothermal method, using metal cyano complex precursors. Both the catalysts were evaluated for CO oxidation activity, and show much improved catalytic activity in their nano form, as compared to those prepared by using conventional synthesis method. $\text{PrCoO}_3\text{-CC}$ shows about 100 % CO conversion with the TOF of 0.11 mmol per gram per unit time at temperature of 250 °C. Enhanced catalytic activity of these nano-materials at higher space velocity is of special significance for such non-noble based catalysts. The most striking feature, however, was their thermal stability, as the materials retain their nano form even after using high temperature calcination, as many nanomaterials are usually synthesized at relatively lower temperatures and show significant sintering even at moderate temperatures. This makes possible to use present nano materials even for other higher temperature applications, by taking the advantage of their thermal stability. The improved catalytic activity of nano perovskites is mainly attributed to their improved surface area and better redox properties, as confirmed with TPR studies. Since synthesis method has prominent effect on properties of perovskites type materials, such improved synthesis offers good possibilities to prepare many other perovskite compositions, likely to show much improved catalytic and other properties. The optimization of these materials with improved compositions through partial substitution and studies for other potential environmental applications is underway, including that for soot oxidation activity. It will also be interesting to study the magnetic and electrical properties of such nano and shape controlled perovskite compositions.

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Notes and references

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