

Thermally stable ruthenium-based catalyst for methane combustion

Nitin K. Labhsetwar^{a,*}, A. Watanabe^b, T. Mitsuhashi^b, H. Haneda^b

^a Environmental Materials Unit, National Environmental Engineering Research Institute (NEERI), Nehru-Marg, Nagpur 440020, India

^b Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 3050044, Japan

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Abstract

Ruthenium shows high thermal stability when incorporated in perovskite type structure. Perovskite type lanthanum ruthenate materials can be synthesized using various improved methods and can be used even for high temperature applications like methane combustion. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ material in supported and un-supported forms has been synthesized using various techniques, mostly used for the first time to synthesize this material. This improved synthesis of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ resulted in improved physical and catalytic properties. This paper reports synthesis of supported and un-supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ materials and laboratory evaluations of their catalytic activity towards methane combustion reaction. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ shows high thermal stability, which could be due to stable 4+ oxidation state of ruthenium and its incorporation in perovskite type structure. Ruthenium based materials show good activity for methane oxidation probably due to intrinsic activity of their ruthenium component.

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1. Introduction

Ruthenium and its oxides are good catalysts for several reactions of commercial and environmental importance. However, ruthenium dioxide (RuO_2) has strong tendency to get oxidized in to higher valence oxides, which are of volatile nature at higher temperature. Incorporation of ruthenium in perovskite structure can substantially improve its thermal stability. We have recently reported improved synthesis of LaRuO_3 , a lanthanum–ruthenium-based perovskite type material with ruthenium in 3+ oxidation state, and its catalytic properties [1]. This material, although shows good catalytic activity especially for oxidation reactions, still suffer thermal degradation above 900 °C, under prolonged exposure in oxidative atmosphere. This could be due to the oxidation of ruthenium to favoured 4+ oxidation state. The high catalytic activity of LaRuO_3 for environmental reactions like methane combustion has prompted us to synthesize thermally stable

lanthanum ruthenate type materials. As 4+ oxidation state is a stable state for ruthenium, lanthanum ruthenate perovskites with Ru^{4+} are expected to show better thermal stability. Almost all the ruthenium present in $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ is in 4+ oxidation state and occupies ‘B’ sites in perovskite structure. This material is first reported in 1980 by Abraham et al., while synthesizing a targeted $\text{La}_2\text{Ru}_2\text{O}_7$ (and not $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$) type pyrochlor at about 900 °C for 48 h in vacuum and using RuO_2 and La_2O_3 as solid precursors [2]. The structural details of this material were reported in this study. No other detailed study on synthesis of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ and no study on catalytic properties of this material are known to the best of author’s knowledge. Our previous work on a series of perovskite type catalytic materials show their potential in environmental catalysis [3–10]. Development of improved synthesis methods especially for their synthesis in supported form can substantially increase their otherwise very low surface area, making them useful catalysts for many practical applications.

High temperature catalytic processes like deep oxidation/combustion of methane, partial oxidation of methane,

* Corresponding author.

E-mail address: nitin_neeri@yahoo.com (N.K. Labhsetwar).

fuels combustion etc have recently attracted many researchers due to their applied importance. Catalytic methane combustion is a relatively cleaner route for production of energy and is associated with low NO_x , CO and HC emissions. This is also becoming attractive for another very important reason of resulting in to about 25% less CO_2 emissions for generating the same amount of energy as compared to coal based power plant. However, the severe application requirements like extreme temperature and high oxidation activity is putting up challenge towards development of practically feasible catalytic materials. Perovskites can be considered as potential materials for this application, mainly due to their thermal stability and tailoring capabilities to design oxidation catalyst for a specific reaction. A number of publications reported the activity of perovskite type catalysts for these reactions [11–22]. Saracco et al. reported the potential of Mg-doped LaMnO_3 type perovskite [18], while Cimino et al. studied the structured perovskites for methane combustion [11]. Isupova et al. also reported the honeycomb supported lanthanum manganate and ferrite type materials and emphasized the importance of thermal stability and also surface area of such catalytic materials for this high temperature reaction [19]. With the inherent catalytic activity of ruthenium in its oxide form and possibility of its stabilization in perovskite structure, these compounds are expected to show potential activity for methane combustion reaction. The only major limitation of perovskite application is their low surface area, however, with the possibility of synthesizing them on thermally stable support materials, make them still more attractive for this particular application. This communication reports the novel synthesis methods of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ material in its supported and un-supported forms and evaluation of their catalytic activity towards methane combustion reaction.

2. Experimental

$\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ has been synthesized following different methods in a view of its easy and possibly cost effective synthesis. Efforts were also made to prepare supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ material to improve its surface area. The details of various synthesis methods used are as follows:

2.1. Synthesis of un-supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$

2.1.1. Co-precipitation method

Most of the reported ruthenium perovskites were initially studied for their structural and physical properties, and solid-state synthesis route was very commonly used to achieve high purity. However, co-precipitation is a versatile method for perovskite synthesis.

The following two solutions were prepared to synthesize 10.0 g of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$:

1. 200 ml lanthanum tri-chloride solution containing 4.426 g of lanthanum
2. 200 ml ruthenium tri-chloride solution containing 3.681 g of ruthenium.

Both the solutions were mixed together and diluted with 100 ml of de-ionized water to make the 500 ml of mixed metal solution. About 800 ml of 2N aqueous ammonia solution is then slowly added to the mixed metal solution at a rate of 100 ml/min and with a stirring of 100 rpm. The co-precipitated mass was allowed to settle for 2 h followed by filtration and washings with de-ionized water. After drying in oven at 70°C for 5 h, the precipitate was heated in a furnace under nitrogen atmosphere (alternatively in air atmosphere) at 400°C for 4 h. The dried mass thus obtained was grinded (90% particles less than $6.0\ \mu\text{m}$), and again heated in air atmosphere, at temperature $900\text{--}1000^\circ\text{C}$ for 8 h to obtain the final product.

Alternatively, the mixed metal ion solution was added to aqueous ammonia solution at a rate of 100 ml/min and with constant stirring of 100 rpm, for the co-precipitation of lanthanum and ruthenium. Subsequently, the final product was obtained by filtration, washing and heating of precipitate, exactly as described above. This sample was designated as LR-1.

2.1.2. Direct heating of mixed metal solution

The limitation of solid-state synthesis process is poor mixing of reactants, which can be effectively avoided by using solutions of reactant precursor metals. In this method, mixed metal solution of La^{3+} and Ru^{3+} was prepared as discussed in method Section 2.1.1.

The solution was evaporated to dryness by heating at 60°C or by rotary/vacuum evaporation or using the freeze drying process. The material thus obtained was initially heated under nitrogen atmosphere at temperature 500°C for 3 h. The solid thus obtained was grinded (90% particles less than $6.0\ \mu\text{m}$), and again heated in air atmosphere, at temperature $900\text{--}1000^\circ\text{C}$ for 8 h to obtain the final product. This sample was designated as LR-2.

2.2. Synthesis of supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$

Due to the high synthesis temperature required for the formation of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ phase, its surface area is always very low. Therefore, efforts were made to prepare supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ using many innovative synthesis routes. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ was synthesized on both alumina powder and cordierite support, considering its applications in environmental catalysis. The alumina powder used was pre-coated with 20 wt.% of La_2O_3 as described elsewhere [1]. Small pieces of cordierite honeycomb with 100–200 psi channel density were also used as supports for $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ synthesis. Small pieces of alumina washcoated honeycomb supports were pre-coated with 20 wt.% of La_2O_3 by repeated impregnation in lanthanum metal solution and subsequent

heating. These lanthana pre-coated cordierite honeycomb and alumina powder were used to prepare supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ as follows:

2.2.1. Using co-precipitated La and Ru hydroxides

The lanthanum and ruthenium were co-precipitated as described in the method of Section 2.1.1. The mixed precipitate was then coated on 50 g pre-coated alumina powder or cordierite honeycomb. A slurry of co-precipitated hydroxides was prepared with about 25 wt.% solid content and cordierite honeycomb support pieces were dip-coated and dried applying hot air or by keeping in oven. This procedure was repeated to obtain about 25 wt.% loading of precipitate on cordierite support. Similarly the mixed precipitate was coated on 50 g pre-coated alumina powder. A slurry of co-precipitated hydroxides was mixed with pre-coated alumina followed by drying by applying hot air or by keeping in oven. This procedure was repeated to obtain about 25 wt.% loading of precipitate on alumina. These precipitate coated support materials were subsequently heated at 900–1000 °C for 8 h in air atmosphere to synthesize $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ on stabilized alumina or cordierite supports. This alumina supported sample was designated as LR-3.

2.2.2. Using in situ method

Mixed metal solution of La^{3+} and Ru^{3+} was prepared as described in method of Section 2.1.1. The mixed metal solution was diluted to 0.5 l by de-ionized water. About 200 g of alumina powder (pre-coated with 25 wt.% of lanthanum oxide) was then impregnated with mixed metal solution following the incipient wetting. The material thus obtained was dried by heating at 70 °C or by rotary/vacuum evaporation. The process was repeated for about 10 times to get approximately 15 wt.% loading of mixed metal precursors (lanthanum chloride and ruthenium chloride). The precursor loaded alumina powder was then heated initially under nitrogen atmosphere at temperature 500 °C for 4 h and subsequently at temperature 900–1000 °C for 12 h to obtain the $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ on alumina. The $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ coated alumina powder thus obtained shows a BET-surface area of approximately 64 m²/g. This sample was designated as LR-4.

2.2.3. Using deposition precipitation method

In yet another improved method, “precipitation from homogeneous solution” technique was used for the synthesis of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ on catalyst supports in powder or honeycomb form. The following two solutions were prepared and mixed together:

- 100 ml lanthanum tri-chloride solution containing 0.4426 g lanthanum.
- 100 ml lanthanum tri-chloride solution containing 0.3681 g ruthenium.

About 10 g of alumina powder pre-coated with 25 wt.% of lanthanum oxide was dispersed in this solution. Fifteen

grams of urea was also added to this mixture and temperature was slowly raised to 90 °C. This was kept for 3 h with constant stirring (about 50 rpm). The mixed hydroxides of lanthanum and ruthenium slowly get precipitated and deposited on alumina. The alumina powder is then separated, washed with de-ionized water and dried in oven at 150 °C for 3 h. Subsequently, this powder is heated at 900–1000 °C for 8 h under the air atmosphere to produce $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ on alumina powder. However, very small amount of impurities of other phases were also observed in XRD analysis. The BET surface area shows a value of 65 m²/g. The same method can also be used similarly for cordierite or wash-coated cordierite honeycomb supports having a pre-coat of lanthanum oxide. This alumina-supported sample was designated as LR-5.

2.3. Characterization of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ samples

All the samples were characterized for chemical composition using both wet chemical analysis and ICP-AES technique. Powder X-ray diffraction data were recorded at room temperature on a Rigaku Rint-2200HF using Bragg–Brentano geometry with Cu K α radiation (40 kV, 50 mA). XRD data were analyzed with Rietvelt Refinement Programme RIETAN-2000 for phase identification and detailed structure determination. Lattice parameters and atomic coordinates were determined for LR-1 sample, while other samples were characterized only for the presence of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ and impurity phases if any. BET surface area of samples was determined following the standard nitrogen adsorption method using Micromeritics ASP-200 instrument. Thermal stability experiments were performed by heating the various materials at temperatures ranging from 1000–1100 °C, under both inert and air atmospheres. These post-heated samples were investigated by XRD and chemical analysis. Thermal stability experiments were also performed using TG technique in the same temperature range, mainly to study the possibility of thermal loss by the formation of volatile ruthenium oxides. These experiments were conducted using Rigaku-TAS-200, Thermal Analyzer, at three different temperatures 900, 1000 and 1100 °C by heating the samples in air atmosphere for 12 h.

2.4. Catalytic evaluations

The LR-1 and LR-5 samples have been investigated for their catalytic activity towards methane combustion reaction because of their relatively better purity as compared to other samples. These catalytic reactions have been carried out using a pure gas laboratory evaluation assembly equipped with precise gas flow control and heating system. Gas analysis was carried out using an auto-sampling PC controlled, MTI-P-200, GC system. The following feed was used for the catalytic evaluation:

methane = 1.5% + O₂ = 18% and balance He.

Two different space velocities (W/F) used for the reaction were approximately 0.8 and 0.09 g s/N cm⁻³.

3. Results and discussion

Depending on the chemical composition of perovskites, co-precipitation can be considered as an effective route to prepare perovskites with high purity. Co-precipitated sample LR-1 was also found to be in pure form. The XRD pattern and Rietvelt refinement results confirm the formation of single phase well crystalline La_{3.5}Ru_{4.0}O₁₃ and the data match well with the previously reported study on same material synthesized through solid-state synthesis route [2]. The BET surface area (Table 1) of this sample is 4.0 m²/g, which is quite low due to the high synthesis temperature. X-ray diffraction analysis of other samples confirms the presence of crystalline La_{3.5}Ru_{4.0}O₁₃ phase with different purity, depending on synthesis method (Table 1). The LR-2 sample also shows reasonably good crystallinity and purity. Efficient mixing of reactant cations possibly at molecular level in solution form can be a favourable condition for perovskite formation as compared to solid-state route. Synthesizing perovskite phase from mixed metal solution is also important, considering suitability of this easy method for bulk production.

Due to low specific surface area of La_{3.5}Ru_{4.0}O₁₃ material, it is necessary to improve the same for its catalytic applications. Preparation of supported La_{3.5}Ru_{4.0}O₁₃ is therefore, necessary as no substantial improvement in surface area can be achieved by attempting lower temperature synthesis, which is also not applicable when the material is targeted for high temperature applications. Our series of investigations [3–7] on preparation of supported perovskites infer the followings:

- Perovskite precursors are generally reactive towards support materials, depending upon the nature of precursors and support.
- It is necessary to prepare a suitable pre-coat on alumina or cordierite supports to prevent their reactivity with perovskite precursors.
- Precursors in ionic solution form shows higher penetration in to support materials and are more susceptible for undesired reactions, as compared to their co-precipitated form.
- Intimate contacts of precursors in co-precipitated form, facilitate perovskite formation, even when dispersed on support materials.

Considering the above findings, we have attempted to prepare La_{3.5}Ru_{4.0}O₁₃ material supported on alumina powder and cordierite pre-coated with lanthanum oxide. The LR-3 sample shows formation of alumina powder supported La_{3.5}Ru_{4.0}O₁₃ phase with reasonably good XRD peak intensities for La_{3.5}Ru_{4.0}O₁₃ phase, however, along with a very small amount of other phases. The pre-coat of lan-

thana on alumina helps in two ways. It improves the thermal stability of alumina while also making it quite inert towards perovskite precursor. Some amount of other phases were also found to be present in this sample, however, coating of co-precipitated precursors on support materials is an easy method to prepare supported La_{3.5}Ru_{4.0}O₁₃. The specific surface area of this sample is 61.0 m²/g, which suggests that more than 15-fold increase in surface area can be achieved by supporting La_{3.5}Ru_{4.0}O₁₃ on pre-coated and pre-heated alumina powder. The LR-4 sample has been prepared by directly contacting support materials with precursor mixed metal ion solution. Despite the presence of lanthana pre-coat on alumina powder, this sample shows relatively poor formation of La_{3.5}Ru_{4.0}O₁₃ phase along with presence of relatively more impurity phases with higher intensities. Although, ionic solution of precursor metals gives best mixing of metal ions to help form the mixed oxides or perovskites, however, as also observed previously [3,4], metal ions in solution can penetrate the support materials and are relatively more reactive. This normally leads to the formation of undesired phases mainly by reaction of these ionic precursors with support materials. Relatively much inert support materials with higher surface area can help overcoming this problem. The specific surface area of this LR-4 sample was 64.0 m²/g, which is almost similar to LR-3 sample.

The LR-5 sample prepared by “deposition precipitation” (DP) method [8] shows relatively much better formation and dispersion of La_{3.5}Ru_{4.0}O₁₃ on support materials. This is in line with our previous studies on supported LaRuO₃ synthesis [1]. The XRD data show relatively better formation of La_{3.5}Ru_{4.0}O₁₃ as compared to other two supported samples. This LR-5 sample can be better compared with LR-3 sample, as in both the cases co-precipitated precursors were deposited on support materials. However, DP method offers rather controlled co-precipitation of precursor metals and their uniform dispersion. This method therefore, is relatively more suitable for the preparation of supported La_{3.5}Ru_{4.0}O₁₃, especially for its preparation on alumina washcoated honeycombs or alumina powder pre-coated with suitable oxides. Controlled and slow co-precipitation of precursor on continuously shaken/moving support makes it possible to achieve uniform dispersion of co-precipitated precursor metal ions. The BET surface area of this LR-5 sample is 65.0 m²/g, which is again quite close to other supported samples.

It is clear from Table 1, that alumina loses its surface area drastically after heating above 800 °C, mainly due to the particle sintering. There was a clear improvement in surface area of post-heated alumina after the pre-coat. The supported La_{3.5}Ru_{4.0}O₁₃ samples were prepared on this pre-coated alumina powder. After formation of La_{3.5}Ru_{4.0}O₁₃ phase, the specific surface area of lanthana pre-coated alumina was found to be decreased from 97 to about 64 m²/g (Table 1), however, this is still several fold higher than un-supported La_{3.5}Ru_{4.0}O₁₃ powder.

Table 1
Characterization of various $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ samples

Sample	Specific surface area (m^2/g)	Phases present				
		$\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$	RuO_2	Ru	La_2O_3	Other
LR-1	4.0	Yes (highly crystalline)	No	No	No	No
LR-2	3.4	Yes (highly crystalline)	Yes (very weak)	Yes (very weak)	No	Yes (weak)
LR-3	61.0	Yes (moderate intensity)	Yes (low intensity)	No	Yes	Yes (weak)
LR-4	64.0	Yes (low intensity)	Yes	Yes	Yes	Yes
LR-5	65.0	Yes (moderate intensity)	Yes (very low intensity)	No	Yes	Yes (very weak with relatively less number of other phases)
γ -Alumina	273	No	No	No	No	Yes
Post-heated alumina	62	No	No	No	No	Yes
Lanthana pre-coated post-heated alumina	97	No	No	No	Yes	Yes

3.1. Thermal stability

Thermal stability of LR-1 sample was studied in detail. The material was first heated in furnace at 1100°C for 24 h under air atmosphere. The XRD analysis of this post-heated sample does not show any appreciable change. To investigate further, this sample was heated under the same conditions, using a TG apparatus. The sample shows very insignificant weight loss on heating for 12 h. This indicates that a very small portion of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ gets decomposed and probably small amount of ruthenium is volatilized in oxide form at higher temperature. Presence of weak lanthanum oxides peaks in post-heated sample suggests the sintered lanthanum oxide impurities after volatilization of ruthenium oxide component. Similar thermal stability experiments were also conducted at 1050 and 1100°C . $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ shows practically no weight loss and no change in XRD patterns after 12 h of heating at 1050 and 1100°C . This material is therefore, stable upto 1100°C under air atmosphere.

This $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ material was also studied for its thermal stability under oxidative atmosphere with increased oxygen concentration, as LaRuO_3 type perovskite material shows oxidation of phase even at 1000°C [1]. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ was heated under continuous flow of oxygen at 1100°C for 12 h. Unlike LaRuO_3 , this material does not show any weight loss or structural changes. This could be due to the presence of ruthenium in 4+ oxidation state, which is quite stable. It could therefore, be inferred that ruthenium can be thermally stabilized by incorporating in to perovskite structure in 4+ oxidation state. Ru^{3+} has strong tendency to get oxidized in to Ru^{4+} , which probably affect its thermal stability (even in perovskite structure) beyond 950°C and especially under the oxygen atmosphere. Almost all the Ru in $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ has 4+ oxidation state and therefore, oxygen partial pressure does not show any significant effect on its thermal stability. The thermal stability of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ phase under air and oxygen atmosphere is remarkable and this material can be used for high temperature applications.

3.2. Catalytic activity for methane combustion

Perovskites in general and lanthanum ruthenate-based perovskites in specific are good oxidation catalysts. Considering this intrinsic activity and its thermal stability under the oxidative atmosphere, this material was investigated for its catalytic activity towards methane combustion. These catalytic evaluations were performed on LR-1 and LR-5 samples due to their better purity in un-supported and supported form respectively. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ was synthesized mainly in view to improve the thermal stability of ruthenate type material, to make them feasible even for high temperature reactions.

The methane conversion efficiency results at two different space velocities for these catalyst samples are presented in Fig. 1. The highest efficiency was observed for the supported sample LR-5 under low space velocity. T_{50} was as low as about 420°C for this sample although, the space velocity was quite low. T_{50} for un-supported sample under the same space velocity was at about 460°C , which indicates that a low temperature mechanism operates for methane oxidation on this perovskite. There was practically no CO generation

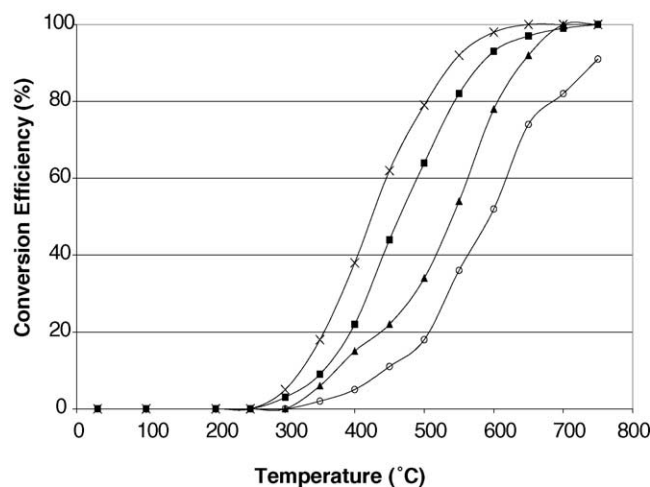


Fig. 1. Catalytic activity of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ for methane oxidation: (■) LR-1, 15 sccm; (○) LR-1, 130 sccm; (▲) LR-5, 130 sccm; (×) LR-5, 15 sccm.

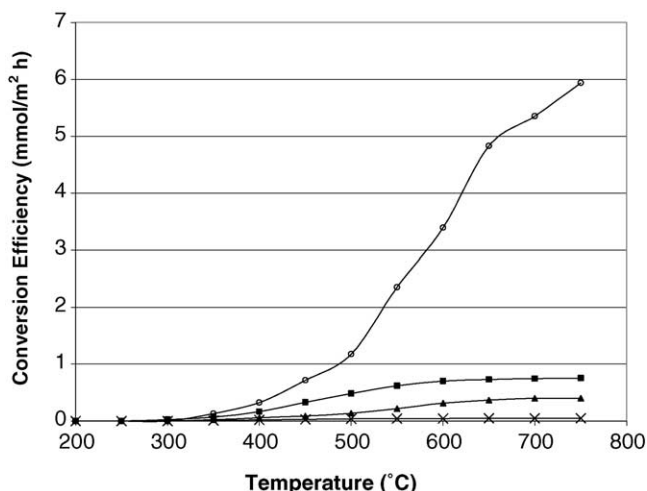


Fig. 2. Catalytic activity of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ for methane oxidation per unit surface area (■) LR-1, 15 sccm; (○) LR-1, 130 sccm; (▲) LR-5, 130 sccm; (×) LR-5, 15 sccm.

and methane was completely oxidized to CO_2 and water. The T_{50} values were substantially increased for the higher space velocity results and the effect of catalyst surface area was again pronounced in this case. Still this effect was less than expected considering almost 17-fold increase in surface area of the supported catalyst LR-5 as compared to that of LR-1. To study this effect more clearly, the results were plotted for the millimoles of methane oxidized per unit surface area (Fig. 2). These results show some interesting findings as un-supported catalyst shows the best performance that to under higher space velocity condition. This indicates that the reaction is kinetically fast and whatever active sites available on this un-supported catalyst are being effectively utilized. Also it indicates that higher surface area of supported catalyst does not necessary mean the proportionate increase in active sites, which are far less than indicated by surface area values obtained. In this way, there is still lot of uncoated surface left on the support material. SEM investigations also support this observation. Although, LR-5 sample was relatively much better in its activity, there still exists scope for the better dispersion of catalyst on support material. This can be expected as perovskites normally has larger particles and is not very suitable for dispersion on alumina.

Fig. 3 shows mmols of methane converted per unit mass of catalyst per unit time. The two bottom curves represent methane conversion on supported and un-supported catalysts under low space velocity. There is some activity improvement with supported catalyst, which is almost diminished at temperature beyond 600°C after which mass transfer becomes insignificant due to low space velocity, while catalyst attains its maximum activity. However, these data clearly shows the advantage of supported catalyst to convert the maximum mmols per unit mass of catalyst. Although, as inferred above, the increase in number of catalyst active sites is less than the expected in relation to the increase in surface area, however, there is still a significant increase in the activity of

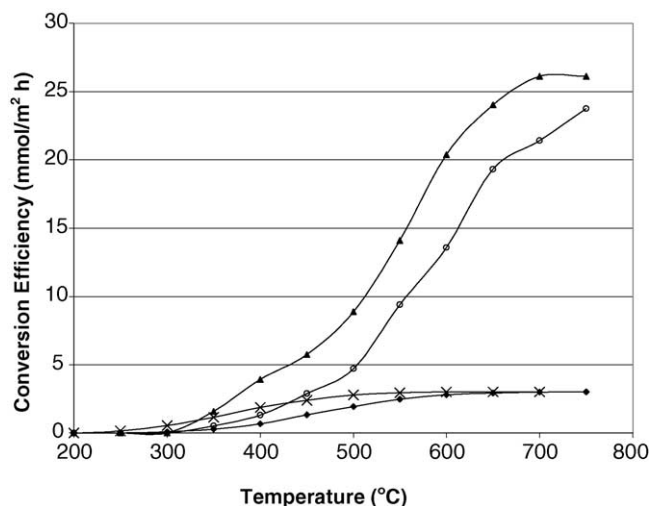


Fig. 3. Millimoles of methane converted on per unit mass of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ catalyst (◆) LR-1, 15 sccm; (○) LR-1, 130 sccm; (▲) LR-5, 130 sccm; (×) LR-5, 15 sccm.

this catalyst. In this way, the supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ material show good catalytic activity for methane combustion to be of practical importance.

3.3. Catalytic mechanism for methane oxidation

The methane oxidation of perovskite type catalysts has been frequently investigated with reference to their redox capacity, substitution on 'A' site to influence the valance of 'B' site cation and thereby improving the oxygen release, or even by chemisorption of oxygen on perovskite surface. These can be broadly explained as described by Pena and Fierro [23].

- 'A' site substitution in perovskite thereby generating either the higher oxidation state of 'B' site cation and release of so called α -oxygen at lower temperature or varying the dimension of the unit cell thereby effecting the covalence of B–O bond or even by creation of structural defects resulting in oxygen mobility.
- Suprafacial reaction of methane with oxygen coming from the oxygen vacancies and refilling up of these oxygen vacancies by the gaseous oxygen. This also is reflected at relatively lower temperature.
- Involvement of structural oxygen of catalyst at higher temperature, which can be considered as intrafacial mechanism.

In this way, it is almost necessary to have 'A' site substitution to achieve oxygen vacancies, which facilitate a suprafacial mechanism and a low temperature methane combustion on perovskite.

The catalytic activity results of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ show a sudden increase in activity after about 450°C , which indicates the importance of intrinsic activity of catalyst at reasonably lower temperature. $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ is an unsubstituted per-

ovskite and does not show any significant oxygen desorption at lower temperature during TPD experiments. The only high temperature peak can correspond to reduction of 'B' site metal ion and release of so-called α -oxygen. It is therefore, interesting to interpret high methane oxidation activity of this material, which could be due to suprafacial mechanism as explained above or through dissociative adsorption of oxygen on catalyst surface. It is unlikely that a redox mechanism works for this reaction on $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ surface. The methane oxidation activity on $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ is much better than the LaRuO_3 type perovskite with Ru in 3+ oxidation state. As there is hardly any difference in the oxygen adsorption-desorption properties of these materials, we suspect that methane adsorption on $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ may also play some role on its catalytic activity. On the other hand, the simple RuO_2 oxide material shows quite similar activity to that of $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ for this reaction. We are investigating this reaction for a few more perovskite type ruthanates having Ru in 4+ oxidation state. Also it is important to investigate the chemical stability of such materials at higher temperature.

In this way, stabilization of ruthenium oxide in perovskite structure can be considered as a thermally stable phase with similar catalytic properties to that of RuO_2 , and it is unlikely that a redox or α -oxygen based mechanism operates for methane oxidation reaction for this material.

4. Conclusion

Our recent work on lanthanum ruthenate perovskites inferred potential catalytic activity of these materials towards certain reactions of environmental importance. Lack of suitable synthesis procedures, low surface area of such perovskite type materials and thermal stability of ruthenium-based catalysts have always been limitations for their catalytic applications. It is possible to stabilize ruthenium in perovskite type matrix, which offers remarkable thermal stability, while use of innovative synthesis methods make possible easy synthesis of both supported and non-supported lanthanum ruthenate type perovskites. Such improved synthesis results in several fold increase in their surface area, thereby making them suitable even for high space velocity applications. Co-precipitation method offers easy method to synthesize high purity $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$, while it has also been possible to prepare supported $\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ using "deposition precipitation" and other innovative techniques.

$\text{La}_{3.5}\text{Ru}_{4.0}\text{O}_{13}$ type lanthanum ruthenate perovskite contains ruthenium almost in 4+ oxidation state and therefore, shows better thermal stability as compared to LaRuO_3 . It shows high catalytic activity for methane oxidation reaction, which is especially important considering the high thermal stability of this material. Such materials need to be explored fur-

ther due to their potential for practical applications as well as to further illustrate their catalytic mechanisms.

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