Abstract—Catalytic combustion of methane has been investigated on transition metal mixed oxide catalysts containing La, Co, Ce or Ag. Catalysts were prepared by the sol–gel citrate method and after characterization, the catalytic activity of the powder catalysts for lean methane fuel were tested in a flow reactor at 60,000 h⁻¹ gas hourly space velocity (GHSV). Reaction products were analyzed by Gas Chromatography equipped with Mass Spectroscopy and Thermal Conductivity detectors. Methane conversions as a function of reaction temperatures (light-off curves) were obtained. Activity ranking of the catalysts were determined based on the light-off curves, and the catalyst with the nominal composition of La₀.₃Ce₀.₁5Co₁.₄O₃±δ showed the best activity in methane combustion with a T₅₀ and T₉₀ temperatures of 353 and 500 °C, respectively. Global reaction kinetic parameters for each catalyst were obtained based on the first order reaction assumption with respect to methane in the case of excess oxygen and activation energies were found to be in between 61 - 69 kJ/mol. It was seen that the addition of Ce increased the activity considerably more than Ag.

Keywords—catalytic combustion, methane, light-off, activity

I. INTRODUCTION

Complete catalytic combustion of methane is achived by using noble metal loaded metal oxide catalysts [1]. Some of the platinum group metals are not only active in hydrocarbon oxidation, they are also active in hydrogen and carbon monoxide oxidation and thats why they are widely studied in gas turbine applications [2]. However, their loss of activity at high temperatures and severe reaction conditions motivated the investigation of alternative materials, like metal oxides [3]. Metal oxides are relatively cheaper than the noble metal based catalysts, but their lower activity creates a disadvantage. Among different metal oxides investigated, perovskite-like metal oxides are promising options.

Perovskites are mixed metal oxides in the form of ABO₃. In this structure, large A cations have 12 coordinations to oxygen atoms and B cations with a smaller ionic radius have 6 coordination to oxygen atoms [4].The elements in the A and B site can be substituted with elements in similar ionic radius, which in turn results in oxygen vacancies in the structure to keep the charge neutrality. This causes an increase in oxygen mobility and catalytic activity. The effect of Mn, Co, and Fe in B position for La based perovskites widely investigated and found very active in methane combustion [5,6].

In this work, perovskite containing mixed oxides with La, Ce, Ag and Co metals were synthesized by sol–gel citrate method to be used in methane catalytic combustion. Ce or Ag metals were used in the A' site in the nominal formula of La₃-xAₓCe₁.x+yCo₁.5O₃±δ.

II. EXPERIMENTAL PROCEDURE

LaₓCeₓCo₁.x+yO₃±δ and LaₓAgₓCe₁.x+yO₃±δ catalysts were prepared by the sol–gel method with the compositions given in Table 1. La(NO₃)₃-6H₂O (Alfa Aesar, 99%), Ce(NO₃)₃-6H₂O (Merck, 98.5%), Co(NO₃)₃-6H₂O (Merck, 99%), AgNO₃ (Merck, 99.8%) precursors salts and citric acid (Merck, 99.5 - 100%) were used as precursors. Required amounts of nitrate forms of the metal salts were weighed based on the nominal composition to be prepared and dissolved in demineralized water. Excess citric acid was added as a complexing agent and pH was adjusted with ammonium carbonate (Merck, 100%). The “sol” obtained was placed in a vacuum rotary evaporator and water was evaporated at 75 °C. The “gel” obtained after evaporation was dried at 120 and 210 °C. Following this, dried material ground and calcined at 700 °C for 5 h.

<table>
<thead>
<tr>
<th>Code</th>
<th>x</th>
<th>y</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>0.9</td>
<td>0.1</td>
<td>Lₐ₀.₉Ce₀.₁₁CoO₃±δ</td>
</tr>
<tr>
<td>Cat-2</td>
<td>0.1</td>
<td>0.4</td>
<td>Lₐ₀.₀₄Ce₀.₁₅CoO₃±δ</td>
</tr>
<tr>
<td>Cat-3</td>
<td>0.1</td>
<td>0.4</td>
<td>Lₐ₀.₄Ag₀.₁CoO₃±δ</td>
</tr>
<tr>
<td>Cat-4</td>
<td>0.1</td>
<td>0.5</td>
<td>Lₐ₀.₄Ce₀.₁CoO₃±δ</td>
</tr>
<tr>
<td>Cat-5</td>
<td>0.1</td>
<td>0.5</td>
<td>Lₐ₀.₄Ag₀.₁CoO₃±δ</td>
</tr>
</tbody>
</table>

After calcination, XRD tests were performed with X-Ray Diffractometer Rigaku D-Max 2200 Series. Cu K-α radiation at λ=1.540562 Å between 2Theta= 5 - 70° was used. Surface area and the pore size distribution of the catalysts were measured with Quanchrome Corporation, Autosorb-1/MS. SEM pictures were taken with JEOL/JSM-6335F/INCA. Temperature-programmed reduction (TPR) and Temperature-programmed oxidation (TPO) experiments were performed using an AutoChem II 2920 (Micromeritics) analyzer equipped with a TC detector. Catalytic activity tests were performed in a quartz flow reactor connected to an on-line GC/MS/TCD. The details of the experimental set-up can be found elsewhere [7].
III. RESULTS AND DISCUSSION

Characterization: X-Ray Diffraction analysis of the catalysts show that all the catalysts prepared contained perovskite phase (LaCoO$_3$, PDF No: 00-048-0123) as well as single metal oxides (Co$_3$O$_4$, PDF No: 00-042-1467 and CeO$_2$, PDF No: 00-034-0394). Cat-3 and Cat-5 contained metallic silver, and no Ag$_2$O phase was seen.

As seen in the Table 2, BET specific surface area of the catalysts range in between 2.73 – 22.21 m$^2$/g. The catalyst with the largest surface area provided the best activity, which will be discussed further in the next section. An interesting note here is that, the small increase in the amount of Ce or Ag caused an increase in the surface area. The compositions La$_{0.9}$Ce$_{0.1}$CoO$_3$$^{\pm \delta}$ and La$_{0.1}$Ce$_{0.4}$Co$_{1.5}$O$_3$$^{\pm \delta}$ prepared in our previous work with a slightly different method also yielded similar results [7]. The mean pore diameter of the catalysts were calculated by using Barett-Joyner-Halendar (BJH) method. Analysis results show that, Cat-1, 3 and 5 have a bimodal distribution with 5 and 30 nm average pore diameters, while Cat-2 and Cat-4 had a mean pore diameter of 18 nm, all indicating a mesoporous character.

Table 2: Surface area and the reaction temperatures at methane conversions of 50 ($T_{50}$) and 100% ($T_{100}$)

<table>
<thead>
<tr>
<th>Code</th>
<th>SSA, m$^2$/g</th>
<th>$T_{50}$, °C</th>
<th>$T_{100}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>3.35</td>
<td>447</td>
<td>650</td>
</tr>
<tr>
<td>Cat-2</td>
<td>16.75</td>
<td>421</td>
<td>600</td>
</tr>
<tr>
<td>Cat-3</td>
<td>2.73</td>
<td>407</td>
<td>600</td>
</tr>
<tr>
<td>Cat-4</td>
<td>22.21</td>
<td>353</td>
<td>500</td>
</tr>
<tr>
<td>Cat-5</td>
<td>6.89</td>
<td>374</td>
<td>550</td>
</tr>
</tbody>
</table>

SEM pictures of the catalysts were taken as prepared without further grinding after calcination, and the agglomerations could easily be seen. The less porous catalyst morphology was observed for Cat-1, 3 and 5 here, in line with BET analysis.

Activity: Catalytic combustion performance is generally evaluated at a constant flow rate for a constant catalyst weight (constant gas hourly space velocity, GHSV) as a function of the reactor wall temperature, by using a fixed bed reactor. Several measures were taken to keep the heat and mass transfer effects to a minimum. The large heat of reaction of methane would cause the temperature on the catalyst surface to be higher than the reactor wall temperature, leading to the heat transfer effects on the reaction rate. This is why methane concentration in the feed was kept very low, to keep the temperature variations in the catalyst bed as small as possible,
allowing us to assume isothermal conditions. Small amount of catalyst, small grains and high space velocity of the fuel lean reaction mixture were used to minimize the external and internal mass and heat transfer effects. Quartz powders were added to dilute the catalyst, and further reduce the heat transfer effects. Methane conversions as a function of reaction temperatures are shown in Figure 3 and the Table 2. $T_{50}$ temperature, the reaction temperature at 50 % conversion, is sometimes called light-off temperature and frequently used to rank the catalysts based on their activity [8]. The lower the $T_{50}$ temperature, the more active the catalyst is. Table 2 lists the reaction temperatures both at 50 and 100% conversions for comparison.

As it is seen in the table, all the catalysts completed the combustion between 500 to 650 °C. Cat-4 with the largest surface area and the crystal phases of LaCoO$_3$, CeO$_2$ and Co$_3$O$_4$ yielded the lowest $T_{100}$ temperature (the temperature at which 100% methane conversion achieved). The activity of Ce or CeO$_2$ containing catalysts is due to the oxygen mobility provided by Ce$^{4+}$ - Ce$^{3+}$ ions during the course of the reaction [9]. It is seen that although Cat-2 had a comparable surface area to Cat-4, its activity is even below the catalyst La$_{0.1}$Ag$_{0.5}$Co$_{1.5}$O$_{3+δ}$ (surface area 6.89 m$^2$/g). Surface area has a large effect on the reaction rate and therefore the activity of the catalysts, yet large surface area does not always mean high catalytic activity. The type of the metals, crystal phases, pore sizes and the distribution of the active phase on the catalyst surface has certainly substantial effect on the catalytic activity as well. Therefore, although Cat-5 had lower surface area and less porosity, its relatively high activity is an indication of the contribution of Ag into the catalytic activity. Cat-3 and Cat-5 reached the $T_{50}$ temperatures (the temperature at which 50 % methane conversion is achieved, which is an indication of light-off region), at 407°C and 374°C. Silver addition increased the catalytic activity in methane combustion, but did not increase it as much as Ce added catalyst compositions.
Figure 2. Light-off curves of the catalysts

It is shown that, the crystal size of the Ag is critical in the activity behavior of the catalyst [10]. Small Ag crystals oxidize into Ag2O form in the existence of oxygen lowering the number of Ag crystals on the surface available for reaction. We calculated Ag crystallite dimensions by using the Scherrer Equation [11] below, based on the strongest XRD diffraction peak of Ag for each Ag added catalyst.

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where, D: Crystal dimension (Å), k: 0.9, \( \lambda \): 1.5405, \( \theta \): Diffraction angle and \( \beta \): Full width at half maximum.

The crystallite sizes of Cat-3 and Cat-5 were calculated as 15 and 31 nm, respectively. Cat-3 with lower crystal size also has lower activity. While the heat of adsorption of small Ag crystallites is 50 kcal/mole, it is about 34 - 41 kcal/mole for larger Ag crystallites resulting in a weaker Ag-O bond [10]. The weaker Ag-O bond leaves more surface available for methane adsorption, which may explain why Cat-5 showed better activity compared to Cat-3 in our tests.

Light-off curves contain the kinetic information that can be extracted from the experimental conversion versus temperature data. They reflect both physical and chemical events that take place, and are very sensitive to the activation energy and frequency factor [12]. Since the reaction mixture is studied under fuel lean conditions, oxygen dependency of the methane combustion rate can be neglected, and reaction order can be assumed as the first order, with respect to methane concentration. With the assumption of isothermal plug flow reactor model, apparent activation energy and pre-exponential factors were obtained from the Arrhenius plots. Apparent activation energy of Cat-4 was lower, in accordance with the higher activity observed for this catalyst experimentally.

IV. CONCLUSION

The effect of Ce and Ag addition into LaM\(_{x}\)Co\(_{2-x}\)O\(_3\) on the catalytic combustion of methane has been investigated. From the activity test results, it is seen that surface area is not directly proportional to catalytic activity of the catalysts tested. Although Cat-4 with the largest surface area has shown the best catalytic activity, Cat-5 with a low surface area gave a comparable activity as well. It is seen that, LaCoO\(_3\) perovskite phase (Cat-1) is not as active in the methane combustion as the mixed oxide catalysts (Cat-2 to 5). The apparent activation energy of the Cat-4 was found as 65.6 kJ/mole. Experimental results show that, Ce substituted La\(_x\)M\(_{1-x}\)Co\(_2\)O\(_3\) catalyst can be a good candidate for methane catalytic combustion.

ACKNOWLEDGMENT

The financial support provided by the Scientific and Technological Research Council of Turkey (TUBITAK, Grant No:106G039) is greatly acknowledged.

REFERENCES