Total Oxidation of Toluene on Nano-Perovskites La$_{1-x}$B$_x$CoO$_3$ (B: Ag, Sr)*

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A series of nanosized perovskite oxides, LaCoO$_3$ and La$_{1-x}$B$_x$CoO$_3$ ($x = 0.1$; B: Sr, Ag), was synthesized by citrate method. The samples were characterized by XRD, IR and SEM. The XRD results show that all samples have principal phase with rhomboheda perovskite structure and particles size of 30-50 nm. The catalytic performance of these nanoperovskites has been evaluated by the total combustion of 1000 ppm of toluene in air. The result obtained shows the highest activity for the sample La$_{0.9}$Ag$_{0.1}$CoO$_3$. The last one seems to be related with the highest quantity of oxygen released as showed by oxygen temperature program desorption results (O$_2$-TPD).

Keywords: Nano-perovskite; Total oxidation; Volatile organic compound; Toluene

I. INTRODUCTION

The release of volatile organic compounds (VOCs) are known to cause air pollution such as photochemical smog, ground level ozone, ozone depletion, sick house syndrome, and chemical sensitivity [1-3]. A number of catalysts have been used for the complete oxidation of VOCs. Generally, they were classified in two groups: supported noble metal and transition metal oxide [4-10]. Supported noble metal as Pt and Pd is well estimated as efficient catalysts for the total oxidation of VOC. However, they are expensive. Therefore, transition metal oxide is attired researcher in recent time. Because this one also shows a good activity and, especially, it is much cheaper. Among them, mixed oxide of transition metal, as perovskite, has more advantages. Since this one not only shows a good activity but also a high thermal and hydrothermal stability. In this word, we prepared a series of perovskites La$_{1-x}$B$_x$CoO$_3$ (B: Ag, Sr) and examined their catalytic activity in total oxidation reaction of toluene which has been chosen as VOC probe molecule because aromatics are present in the industrial and automotive emission [11, 12]. The partial substitution of Co by Ag or Sr was expected to improve catalytic activity of LaCoO$_3$ which is known as the most active catalyst in perovskite group for total oxidation of VOC.

II. EXPERIMENTAL

A. Catalyst preparation

Series of perovskite La$_{1-x}$B$_x$CoO$_3$ was prepared by citric method [13]. All used chemical compound have analysis purity. Firstly, nitrate salt (Co(NO$_3$)$_3$, La(NO$_3$)$_3$, AgNO$_3$ and citric acid C$_6$H$_5$O$_2$ were dissolved each other in an adequate amount of H$_2$O. Then, they were mixed with stirring for 30 minutes before being evaporated in rotary evaporator to obtain a resin. This one was dried at 80°C in oven and then, calcined at 600°C for 5 hour.

B. Catalyst characterization

All prepared samples were characterized by different methods: X-ray diffraction, scanning electronic microscopy (SEM), BET surface measurement, and temperature programmed desorption of oxygen (TPD-O$_2$).

The crystalline phases were examined by X-ray diffraction using D8 Advance Bruke diffractometer with CuKa irradiation source ($\lambda=0.15406$ nm) operated at 40 kV and 30 mA. The XRD measurement was performed with 0.03° step per second, from 20° to 70° (2θ).

SEM images of sample were taken by using JEOSJSM-5410 LV Scanning Electron Microscope. The BET surfaces were determined by using AutochemII.

The TPD-O$_2$ was performed using Micromeritics Autochem II. The samples were activated in O$_2$ (10 vol%)/He at 200°C for 1 hour then cooled to ambient temperature and purged in He flow. The measurements were carried out from room temperature to 700°C.

C. Catalytic tests

Catalytic activity of all samples was estimated by total oxidation of toluene. Toluene was mixed in air to obtain a flux at 1000 ppm of toluene concentration. The organic products were determined by Chromatography HP 6280 equipped FID detector, and the formation of CO$_2$ was detected by TCD detector.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns are presented in Fig.1. Principal phases recognized rhomboheda perovskite phase...
for all samples. In case La$_{0.9}$Ag$_{0.1}$CoO$_3$, presence of metallic silver was determined (2$\theta$ = 38.1, 48.2$\deg$). Certainly, this one was formed by decomposition of Ag(NO$_3$)$_2$. It is possible that an amount of Ag$^+$ wasn’t substituted or/and incorporated in perovskite phase.

In order to understand well their structure, these samples were characterized by IR. Figure 2 showed results obtained. We observed characteristic peaks for perovskite structure such as 593.3, 562.7, 417.8 cm$^{-1}$. In case of sample substituted by Ag and Sr, a shoulder peak was recognized at 642 cm$^{-1}$. This one was characteristic for phase Co$_3$O$_4$ [15]. Thus, it is possible that when a small amount of Ag$^{+}$ or Sr$^{2+}$ was incorporated in perovskite structures of LaCoO$_3$, a small amount of Co$^{2+}$,Co$^{3+}$ was pushed out of perovskite structure and formed phase Co$_3$O$_4$. However, this phase may be formed in form of cluster and/or well dispersed on perovskite phase.

Figure 3 presents the SEM image of all samples. It was noted that all samples consisted of nano particles with diameter in range of 30-50 nm. The particles were in spherical form and quite uniform.

Figure 4 presents the results TPD-O$_2$. Generally, it was noted that there were two type of oxygen desorbed [16]: O$_2$ (oxygen desorbed at temperature below 500$\deg$C) and O$_2$ (oxygen desorbed in range of temperature from 500-700$\deg$C). For the sample LaCoO$_3$, it is obvious that there are three desorption peaks of O$_2$ at 441$\deg$C, 599$\deg$C and 713$\deg$C. Among them, the peak at 441$\deg$C was three times more intense than two others. A much more intense peak at 426$\deg$C was observed for La$_{0.9}$Sr$_{0.2}$CoO$_3$. In the range of higher temperature, oxygen continued to desorbs but no shape peak was found. It seems that there were several peaks but they appeared continuously with a small difference of temperature. However, it is seen that the adsorption of O$_2$ is shifted at lower temperature. In case of La$_{0.9}$Ag$_{0.1}$CoO$_3$, a small peak at 190$\deg$C appeared more sharply in comparison with the precedent case. The second peak was at 471$\deg$C, but it seems that this one was constituted by different peak, because it was obvious that there were two shoulder-peaks at 420$\deg$C, and 600$\deg$C. The third peak, most intense, was shifted at 774$\deg$C. This result was quite in accordance to observation of S.Ifrah et al.[17] These curves were not normalized in weight. Hence, in order to have a qualitative estimation, it is necessary to
report the BET surfaces and quantity of mobile oxygen per gram or square meter of sample as showed in Table 1. It is seen that the substituted sample showed a BET surface quite low than non-substituted sample.

The result of catalytic test was presented in Fig. 5. To compare activity of catalyst, we used two factors, T_{50} and T_{90}, which are values of temperature where 50% or 90% of reactive is converted respectively.

For T_{50}, the diminution of activity was classified as following: La_{0.9}Sr_{0.1}CoO_{3} ≈ La_{0.9}Ag_{0.1}CoO_{3} > LaCoO_{3}. In case of T_{90}, it is clearly found that La_{0.9}Ag_{0.1}CoO_{3} showed a highest activity: La_{0.9}Ag_{0.1}CoO_{3} > La_{0.9}Sr_{0.1}CoO_{3} > LaCoO_{3}. Generally, La_{0.9}Ag_{0.1}CoO_{3} showed slightly higher activity than La_{0.8}Sr_{0.2}CoO_{3} and activities of substituted samples were clearly higher than pure LaCoO_{3}. This properties of substituted perovskites were observed by the group of S. Kaliaguine in case of La_{1-x}A'^{3+}BO_{3} (A' = Sr, Ce, B = Co, Mn) used for the CH oxidation reaction [18]. In our case, basing on TPD-O_{2} result (Table 1), it seems that the catalytic activity was proportional with the quantity of mobile oxygen in bass temperature range (100°C - 200°C). The quantity of mobile oxygen released in higher range of temperature do not have an important role for total oxidation of toluene if we were noted that, up to 200°C, almost of toluene was converted for all catalysts. It was obvious that there was a quick diminution of catalytic activity after the beginning of toluene conversion. This one is in order of LaCoO_{3}, La_{0.8}Sr_{0.2}CoO_{3} and La_{0.9}Ag_{0.1}CoO_{3}. The diminution was possibly due to deposition of coke which blocked catalytic center on catalyst surface. The substitution of Ag or Sr seems to decrease this one.

### IV. CONCLUSIONS

A series of perovskites La_{1-x}B_{2}Co_{3} (B: Ag, x = 0.1; Sr, x = 0.2) was synthesized by citrate method. They were constituted by nano-particles with the diameter from 30 to 50 nm. Perovskite La_{0.9}Ag_{0.1}CoO_{3} showed a highest activity in total oxidation of toluene. Based on TPD-O_{2} measurement, it seems that their activity is proportional with quantity of mobile oxygen on surface in basic range of temperature, from 100°C to 200°C. This result is very potential for the total oxidation of VOC at low temperature.

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