

Preparation and characterization of LaCoO_3

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ABSTRACT

The aim of this research work was to prepare the efficient catalyst to purify pollutant output gases such as SO_2 , NO_2 and CO. This catalyst, lanthanum cobaltate (LaCoO_3) was prepared by the proper method in the analysis laboratory of Tabriz Oil. The first materials were chosen through calcination operation and the temperatures of operation related to the Tamman temperature, therefore the basis for the first material of catalyst was nitrate and aqueous and since we had no availability to lanthanum nitrate, lanthanum oxide was used to prepare the nitrate one. Before all else, the first materials of catalyst were mixed together with the equal mole proportions and then, at the lower and upper temperatures of Tamman temperature, calcination operation was performed. To determine the molecular structure, the XRD analysis was utilized and specified that prepared lanthanum cobaltate was sixth aqueous and had the crystal structure type Triclinic.

Key words: Catalyst preparation, XRD analysis, Tamman temperature, Calcination operation.

INTRODUCTION

LaCoO_3 has presented a vast interest because of its special electrical, magnetic and catalytic properties¹⁻⁴. The catalyst LaCoO_3 can be prepared by means of several methods such as spray drying, freeze drying and also co-precipitation⁵⁻¹². Some methods including hydrothermal, sol gel and citrate¹³ This material usually has been synthesized by ceramic method and certainly the high temperature for the calcination operation¹⁴. Lanthanum catalysts have been researched because of having such an active state¹⁵. One of the unique properties of this catalyst is the simultaneous conversion of pollutant elements. Nowadays CO oxidation has important applications in environment protection, such as indoor air cleaning and automotive exhaust treatment. LaCoO_3 is one of the most important catalysts for CO oxidation. It has been reported that the properties of the catalyst could be improved effectively by controlling its morphology¹⁶⁻¹⁷. There are a lot of applicable properties show the significance of catalyst LaCoO_3 ¹⁷⁻²¹. According to these useful properties, we tried to prepare this

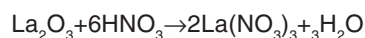
catalyst by the method described below. XRD analysis was utilized to characterize the prepared catalyst.

MATERIAL AND METHODS

Preparing precursor

In fact in this step, by mixing proper chemical compounds, structure of final catalyst would be obtained. Precursor, in microscopic scale has sufficient tissue for ultimate catalyst. To prepare the precursor, the first materials of catalyst LaCoO_3 , lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were used. The reasons of using aqueous and nitrate states of lanthanum and cobalt for preparing precursor were the elimination of water molecules and oxidation of nitrate ions (NO_3^-) in the solid analysis stage through the calcination operation and finally making pores in the bulk of catalyst. The used lanthanum nitrate in this project was obtained through the reaction of nitric acid solution with weight fraction 0.7 and purity percent 99.9% and lanthanum oxide with purity percent 99.99%. To make sure about happening perfect reaction between nitric acid and lanthanum

oxide, nitric acid was used 20 percent more than the stoichiometric value. The reaction of preparing lanthanum nitrate was:



For the next step, separating lanthanum nitrate from the solution, the crystallization operation was performed, for this purpose we used evaporation and supersaturating methods. So the solution of reaction was heated for 4-5 weeks slowly until separation of lanthanum nitrate by evaporation and supersaturating methods. Then the prepared crystal was put in the strainer at 100-120 Celsius degrees for 12 hours till separation of the unbonded water. After drying of the lanthanum nitrate, it was milled in the miller type" Ball Mill" until preparing the 300 meshed particles. For preparing the first mixture of LaCoO₃ catalyst, after milling, the aqueous cobalt nitrate (CO (NO₃)₂.6H₂O) with the purity percent 0.99 was mixed with aqueous lanthanum nitrate (La (NO₃)₃.6H₂O) with the same mole proportions and consequently the next operation would be begun.

Calcination operation

The desirable aims for calcination operation are:

- ' Obtaining the specific structure for active agents or catalyst-based.
- ' Simultaneous controlling of tissue, surface and porous volume.
- ' Achieving proper mechanical resistance.

The next step for preparing catalyst was the calcination operation. Because this step was so significant for plasticizing final catalyst s structure, comprehensive investigations were executed about the optimum temperature, and finally the desirable temperature for the calcination operation were chosen by measuring the Tamman temperature. Among the assumptions we had, the plasticity of tissue and catalyst s structure was happened by mass transfer phenomena in or on the surface of particle or passing through the gas film. These transfers were the driving force for sintering and important around the Tamman temperature. As we knew the Tamman temperature is equal to half of solid melting absolute temperature²².

For measuring the Tamman temperature, cobalt nitrate (CO (NO₃)₂.6H₂O) and lanthanum nitrate (La (NO₃)₃.6H₂O) were mixed in the ceramic crucible and heated in the electric furnace. The melting point of catalyst mixture was determined 1900 °c and therefore Tamman temperature was obtained approximately:

$$\text{Tamman temperature} = \frac{1900 + 273}{2} = 1086^\circ \text{ k} = 813^\circ \text{ c}$$

After obtaining the Tamman temperature, the calcination operation was performed in two separable steps and two temperatures more and less than Tamman temperature in about the same range. The first calcination operation was done at 750° c and the second at 850 °c. Hence, three separate samples of catalyst mixture were transferred to the ceramic crucible after accurate weighing and calcination operation was executed in the electric furnace. Choosing of three mixtures with the same compositions was for eliminating probable errors through the experiments and the same operation was performed to all of these samples. Thorough the calcination operation, the weight of samples dwindled, and it was because of losing the bonded water molecules and the nitrogen of nitrate ions oxidation (NO₃⁻).

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD analysis was employed to test the prepared lanthanum nitrate and the result showed that product was aqueous lanthanum nitrate type (La (.6O). As we compared the figures we simply realized that the prepared catalyst had the Triclinic structure. The figure of lanthanum nitrate obtained from the XRD analysis was shown by Fig. 1:

The data and experimental results were given. As we see, the proportion of weight loss for calcinated catalyst to the first mixture was about 0.37 that determined the preparing of LaCoO₃ catalyst. To confirm this theory, some of the prepared catalyst was analyzed with XRD test after milling so that we could simply recognize the prepared catalysts structure. The XRD pattern showed that the prepared catalyst had the molecule structure of LaCoO₃ and also had the high crystallinity. These

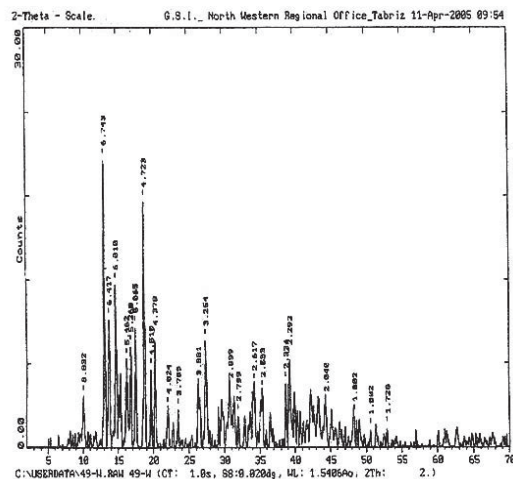


Fig. 1: XRD pattern of lanthanum nitrate

properties demonstrated that this operation was efficient and proper for preparing the catalyst.

After the calcination operation, the process of preparing catalyst completed and the catalyst could be used after reduction. The XRD pattern of the prepared catalyst was given by Fig. 2:

The steps of preparing the catalyst were brought briefly

- A) Preparing lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) from the reaction of nitric acid with La_2O_3 .
- B) Crystallization
- C) Drying of the crystals ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$)
- D) Milling
- E) Preparing the mixed catalyst and adding cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- F) Two different calcination operations at two different temperatures.
- G) The final product.

The Data and Experimental Results of Preparing ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and Catalyst LaCoO_3 : = 25 gram

The volume of nitric acid 70%= 36 cc

Consumed distillate water = 120 cc

Prepared ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) after drying = 65.32

Calcination Operation:

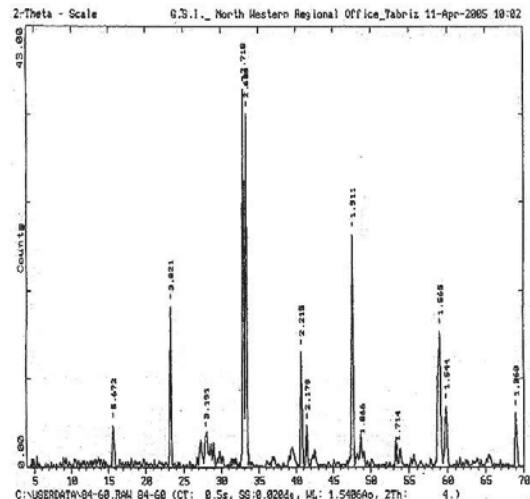


Fig. 2: XRD pattern of the prepared catalyst

Sample 1

Consumed ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) = 9.39 gram

Consumed ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) = 10.66 gram

Catalyst s weight after calcination operation = 7.50 gram

The proportion of catalyst after calcination to the

$$\text{same mixture before calcination} = \frac{7.50}{9.39 + 10.66} = 0.37$$

Sample 2

Consumed ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) = 7.05 gram

Consumed ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) = 8.00 gram

Catalyst s weight after calcination operation = 5.50 gram

The proportion of catalyst after calcination to the

$$\text{same mixture before calcination} = \frac{5.50}{7.05 + 8.00} = 0.37$$

Sample 3

Consumed ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) = 4.70 gram

Consumed ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) = 5.33 gram

Catalyst s weight after calcination operation = 3.70 gram

The proportion of catalyst after calcination to the

$$\text{same mixture before calcination} = \frac{3.70}{4.70 + 5.33} = 0.37$$

CONCLUSIONS

This project concentrated on preparing the efficient catalyst to purify pollutant output gases from "incinerator" furnace. The prepared catalyst could be able to convert the gas elements SO_2 , NO_2 , and CO with the proper reductive gases such as NH_3 , CO and H_2 to the inactive mixtures of sulfur, nitrogen and carbon dioxide. The active materials for catalytic converter consisting of LaCoO_3 were prepared by means of a systematic method in the laboratory. By choosing right chemical materials and series of unit operations, preparing the desirable catalyst that could have ability to eliminate the output pollutant gases, would be done. To confirm the molecular structure, XRD test was done. The result of test

showed that the prepared catalyst was LaCoO_3 and had crystal structure. The calcination temperature was obtained, based on Tamman temperature. With respect to XRD analysis, it was determined that using Tamman temperature was proper for calcination operation and catalyst's character satisfied our aims.

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REFERENCES

1. L. C. Moreno-Aldana, J. M. Rendón and J. S. Valencia, "Structural and morphological characterization of LaCoO_3 and LaMnO_3 perovskites prepared by the citrate method Laboratorio", 11th international conference on advanced materials, Rio De Janeiro Brazil (2009).
2. R. Lago, G. Bini, M. A. Peña, J. L. G. Fierro, "Partial oxidation of methane to syngas using LnCoO_3 perovskites as catalyst precursors" *J. Catal.* **167**: 198-209 (1997).
3. M. A. Peña, J. L. G. Fierro, "chemical structures and performance of perovskite oxides" *Chem. Rev.*, 101: 1981-2017 (2001).
4. Lin Huang; Bassir Mahbod ; Bousselham Echchahed ; Kaliaguine Serge "Comparative studies on the properties of new and conventional perovskite-type LaCoO_3 " **78**: 1450-1456 (2005).
5. Nakayama Susumu, Nippon Kagaku Kaishi, "Perovskite Oxide LaCoO_3 Prepared by Solid-state Reaction, Pyrolysis of a Co-Precipitated Precursor or Pyrolysis of a Heteronuclear Complex" **3**: 485-488 (2002).
6. Keshavaraja A. and Ramaswami AV, 1994. "A comparative study of LaCoO_3 prepared by various wet chemical methods", *Indian J Eng Mater Sci*, 1: 229-236 (1994).
7. M.A. Senaris-Rodrigues and J.B. Goodenough, " LaCoO_3 Revisited " *J. Solid State Chem.* **116**: 224 (1995).
8. M. Popa and M. Kakihana, "Synthesis of lanthanum cobaltite (LaCoO_3) by the polymerizable complex route" *Solid State Ionics.* **151**(1-4): 205-211 (2002).
9. M. Popa, J. Franti and M. Kakihana, "Characterization of LaMeO_3 (Me: Mn, Co, Fe) perovskite powders obtained by polymerizable complex method" *Solid State Ionics* 154–155; 135 (2002).
10. H. Taguchi, S. Yamada, M. Nagao, Y. Ichikawa and K. Tabata, "Synthesis of perovskite-type ($\text{La}_{1-x}\text{Ca}_x$) CoO_3 at low temperature using ethylene glycol and citric acid" *Mater. Res. Bull.*, **37**: 69 (2002).
11. Y. Zhu, R. Tan, T. Yi, S. Ji, X. Ye and L. Cao, "Preparation of nanosized $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ via $\text{La}_{1-x}\text{Sr}_x\text{Co}(\text{DTPA})\cdot 6\text{H}_2\text{O}$ amorphous complex precursor" *J. Mater. Sci.*, **35**: 5415 (2000).
12. H. Taguchi, H. Yoshioka and M. Nagao, "using of perovskite-type LaCoO_3 using poly(acrylic acid)" *J. Mater. Sci. Lett.*, **13**: 891 (1994).
13. Sonya. Ivanova, Ekaterina Zhecheva, and Radostina Stoyanova, "Microstructure of LaCoO_3 prepared by freeze-drying of metal-citrate precursors revealed by EPR" 168-174 (2006).

14. S. Nakayama, M. Okasaki, Y. L. Aung, M. Sakamoto, "Microstructure of LaCoO_3 prepared by freeze-drying of metal-citrate precursors revealed by EPR" *Solid State Ionics*, **158**: 133-137 (2003).
15. Kenji Ichimura, Yasunobu Inoue, and Iwao Yasumori, "Active State of The Catalyst LaCoO_3 ". A Reply to The Comment "Hydrogenolysis and Hydrogenation of Ethylene on LaCoO_3 ." *Bull. Chem. Soc. Jpn.*, **54**: 1787-1792 (1981).
16. S.S. Wong, A.T. Woolley, E. Joselevich, C.L. Cheung, C.M. Lieber, J. Am., "Covalently-Functionalized Single-Walled Carbon Nanotube Probe Tips for Chemical Force Microscopy" *Chem. Soc.*, **33**,: 557-8558 (1998).
17. Fei Teng, Shuhui Liang, Buerger Gaugeu, Ruilong Zong, Wenqing Yao, Yongfa Zhu, "Carbon nanotubes-templated assembly of LaCoO_3 nanowires at low temperatures and its excellent catalytic properties for CO oxidation" *Catalysis Communications*. **8**: 1748-1754 (2007).
18. Jinjun Shi, Ruoxue Yan, Yongfa Zhu, Xinrong Zhang, "Determination of NH_3 gas by combination of nanosized LaCoO_3 converter with chemiluminescence detector" *Talanta*, **6**: 157-164 (2003).
19. Gian Luca Chiarello, Davide Ferri, Jan-Dierk Grunwaldt, Lucio Forni, Alfons Baiker, "Flame-synthesized LaCoO_3 -supported Pd 2. Catalytic behavior in the reduction of NO by H_2 under lean conditions" *Journal of Catalysis* **252**: 137-147 (2007).
20. Yongfa Zhu; Ruiqin Tan; Jie Feng, Shishan Ji, Lili Caob, "The reaction and poisoning mechanism of SO_2 and perovskite LaCoO_3 film model catalysts". *Applied Catalysis A: General*. **209**: 71-77 (2001).
21. V.V. Srdi, L. Nikoli, V. Pejovi, "Strontium-Doped LaCoO_3 Perovskites in solid oxide fuel cells", *Journal of Optoelectronics and Advanced Materials*, 337-341 (2003).
22. J.F. Lepage, "Applied Heterogeneous Catalysis: Design Manufacture, Use of Solid Catalysts", Iran university of science and technology press (2001).