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The effect of preparation: Pechini and Schiff base methods, on adsorbed oxygen of $LaCoO_3$ perovskite oxidation catalysts

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Abstract

$LaCoO_3$ prepared by the sol–gel method using a novel Schiff base complex has a superior property of high ratio of adsorbed oxygen to lattice oxygen to that prepared by the citrate complex-Pechini method. The as-prepared gels, characterized by Fourier transform infrared spectroscopy (FTIR), showed that both lanthanum and cobalt formed complexes before calcination. The IR spectra revealed that $CO_3{}^{2-}$ and $NO_3{}^{-}$, generated on the sample surfaces during heat treatment, could form gaseous compounds and leave vacant sites for oxygen to adsorb. Ratios of adsorbed oxygen (α) to lattice oxygen (β), quantified by X-ray photoemission spectroscopy showed that $LaCoO_3$ prepared by the Schiff base complex method produced higher ratios than that prepared by the citrate complex-Pechini method. A DRIFTS study of toluene oxidation on $LaCoO_3$ showed that small size perovskites without impurity and with a high ratio of adsorbed oxygen (α) to lattice oxygen (β) performed well. $LaCoO_3$ prepared by the Schiff base complex showed higher catalytic activity than that prepared by the citrate complex-Pechini method due to the higher ratio of adsorbed oxygen (α) to lattice oxygen (β).

Keywords: $LaCoO_3$ perovskite; Adsorbed oxygen; Lattice oxygen; Pechini; Schiff base

1. Introduction

Perovskite type oxides are effective in catalytic oxidation. In particular, the activity of $LaCoO_3$ perovskite is comparable to that of Pt/Al_2O_3 [1,2]. $LaCoO_3$ can also be used as a gas sensor and in dry cell electrode materials for high-temperature solid oxide fuel cells [3,4].

It has been assumed that the most important contributions to the high activity of mixed oxides such as the perovskites, represented by ABO_3 (A: the large ion in the dodecahedral hole and B: the transition metal ion) is distortion in the individual BO_6 octahedra [5–7]. The transition metal B in perovskites can be particularly active in oxidative catalysis if it can fluctuate between two stable oxidation states [8]. In this way it is possible to balance electrically: (1) the insertion of O^{2-} ions into a lattice from gas phase O_2 and (2) the formation of oxygen radicals which can be bound to a reactant such as a hydrocarbon from lattice oxygen.

Two types of oxygen are considered to participate in desorption of oxygen on oxidation from the outermost layers of the perovskite structure [8]. The α oxygen is oxygen adsorbed on the catalytic surface. It is accommodated in the $O_2{}^{-}$ vacancies formed (1) by partial substitution of A-site cations by lower valence ions or (2) by vacancies of B-site cations, and involves diffusion of $O_2{}^{-}$ ions through the lattice with the formation of neighbouring high valent metal ions. This α-form is believed to be more active and reacts with hydrocarbons at lower temperature than the lattice oxygen (β). The second, β-oxygen, is observed in the lattice for substituted as well as unsubstituted samples. The diffusion of this type of oxygen inside the lattice is accompanied by diffusion of A and/or B ions and is therefore activated at higher temperatures in relative to α-oxygen.

Such lattice defects cause some modification of the chemical and transport properties and affect the catalytic properties. During the catalytic reaction, a perovskite with a nonstoichiometric composition often exists. Typically a surface oxygen vacancy

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can form active species capable of oxidation reactions by adsorbing oxygen from the gas phase [6]. Oxygen adsorption from gas phase and further incorporation of oxygen atoms into the lattice, usually lead to three charged oxygen species, namely; O_2^-, O^-, and O^{2-}, depending on predominant vacant sites [8]. Oxygen species participating in catalytic reactions involve both the adsorbed oxygen (α) and the lattice oxygen (β) [8].

To prepare a perovskite for catalysis requires materials with redox activity [9]. Currently, common approaches to prepare perovskite type oxides use a sol–gel process [10–12], coprecipitation [10,13,14] or solid-state thermal decomposition [11]. During preparation, the reactants must be mixed at the molecular level. Some work has been done on altering the adsorbed oxygen (α) and lattice oxygen (β) equilibrium by altering the metal A/B ratio in the perovskite lattice [8].

This study relates to the effect of two different sol–gel preparative routes on the adsorption of oxygen on $LaCoO_3$ perovskite. In the well-known Pechini method [15], citric acid is used to coordinate metal ions and ethylene glycol is a solvent for process of polymerization between citric acid and ethylene glycol to format a polyester type resin. The formation of $LaCoO_3$ perovskite in the presence of an *in situ* complexing agent such as an aromatic Schiff base [*N*,*N*′-bis(salicylidene)ethylenediamine] was studied for comparison. Fourier transform infrared spectroscopy was used to investigate perovskite formation and X-ray diffraction was used to characterize the structure and particle size of the perovskite samples. Infrared spectroscopy of adsorbed molecules, known as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), was used to investigate *in situ* reactions on the catalyst surface through monitoring spectral features of the adsorbed molecules [16]. The $LaCoO_3$ perovskites prepared by both sol–gel methods were used for the low temperature oxidation of toluene, a representative aromatic compound in chemical waste effluent. To minimize chemical pollution, catalytic oxidation at low temperature would be important from an economical point of view compared to an incineration process. The interaction between toluene and $LaCoO_3$ on the surface could be observed and related to changes of the catalytic performance. The adsorbed oxygen (α) and the lattice oxygen (β) of the perovskite samples were measured by X-ray photoemission spectroscopy.

2. Materials and methods

2.1. $LaCoO_3$ preparation

2.1.1. The Pechini method (PN) [15,17]

Cobalt nitrate, $Co(NO_3)_2{\cdot}6H_2O$ (99%, Univar), (2.1827 g, 7.50 mmol) was mixed with citric acid (4.7282 g, 22.50 mmol) at a molar ratio of cobalt ion:citric acid = 1:3. Lanthanum nitrate, $La(NO_3)_3{\cdot}6H_2O$ (99.0%, BDH) (3.2476 g, 7.50 mmol) was added to the mixture which was then stirred and slowly heated to 363 K. Ethylene glycol was then added to give molar ratio of 2:3 with the citric acid. The resulting mixture was heated under reflux for 3 h to accelerate the polyesterification reaction of citric acid with ethylene glycol and then heated to remove excess water, giving a resin which was then dried and calcined by the method described below to produce the perovskite oxide (sample LC-PN in Table 1).

Table 1

Sample codes of the prepared catalysts assigned according to heating conditions

Sample	Heating temp (K)	Condition		Sample code
		Gas	Hold up time (h)	
PN	383	Air	12	PN383-12
La-PN	383	Air	12	La-PN383-12
Co-PN	383	Air	12	Co-PN383-12
LC-PN	383	Air	12	LC-PN383-12
LC-PN	423	N_2	3	LC-PN423-03
LC-PN	473	N_2	3	LC-PN473-03
LC-PN	523	N_2/O_2	3	LC-PN523-03
LC-PN	573	N_2/O_2	3	LC-PN573-03
LC-PN	623	N_2/O_2	3	LC-PN623-03
LC-PN	773	N_2/O_2	3	LC-PN773-03
LC-PN	773	N_2/O_2	8	LC-PN773-08
LC-PN	823	N_2/O_2	3	LC-PN823-03
LC-PN	873	N_2/O_2	3	LC-PN873-03
LC-PN	973	N_2/O_2	8	LC-PN973-08
SB	383	Air	12	SB383-12
La-SB	383	Air	12	La-SB383-12
Co-SB	383	Air	12	Co-SB383-12
LC-SB	383	Air	12	LC-SB383-12
LC-SB	423	N_2	3	LC-SB423-03
LC-SB	473	N_2	3	LC-SB473-03
LC-SB	523	N_2	3	LC-SB523-03
LC-SB	573	N_2/O_2	3	LC-SB573-03
LC-SB	623	N_2/O_2	3	LC-SB623-03
LC-SB	773	N_2/O_2	3	LC-SB773-03
LC-SB	773	N_2/O_2	8	LC-SB773-08
LC-SB	823	N_2/O_2	3	LC-SB823-03
LC-SB	873	N_2/O_2	3	LC-SB873-03
LC-SB	973	N_2/O_2	8	LC-SB973-08

A reference gel was prepared by the previous method without adding any metal precursors and was assigned as PN. A gel with a La-precursor, by the method described above but with the addition of $La(NO_3)_3$ only was assigned as La-PN. A gel with a Co-precursor prepared by the method described above but with the addition of $Co(NO_3)_2$ precursor only, was assigned as Co-PN. The abbreviations of the prepared samples were assigned as shown in Table 1.

2.1.2. The Schiff base method (SB)

Salicylaldehyde and ethylene diamine were used to form the Schiff base [*N*,*N*′-bis(salicylidene)ethylenediamine] *in situ*; $La(NO_3)_3$ and $Co(NO_3)_2$ were added for complexation at a molar ratio of Schiff base: cobalt ion: lanthanum ion = 3:1:1 [18]. Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$ (99%, Univar)] (2.1827 g, 7.50 mmol) was mixed with salicylaldehyde (5.4984 g, 45.01 mmol) at a molar ratio of 1:6. Lanthanum nitrate, $La(NO_3)_3{\cdot}6H_2O$ (99.0%, BDH) (3.2476 g, 7.50 mmol), was then added. The mixture was stirred and slowly heated to 328 K and then ethylenediamine was added at a molar ratio of ethylenediamine: salicylaldehyde = 2:3. Drying the product at 383 K gave gel LC-SB.

A reference gel (SB) was prepared by the described method without adding any metal precursors. A gel with a La-precursor