Available online at www.sciencedirect.com

ScienceDirect

Applied Catalysis A: General 311 (2006) 204–212

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

$LaCo_{1-x}Cu_xO_{3-\delta}$ perovskite catalysts for higher alcohol synthesis

N. Tien-Thao [a], H. Alamdari [b], M.H. Zahedi-Niaki [a], S. Kaliaguine [a,*]

[a] *Department of Chemical Engineering, Laval University, Que., Canada G1K 7P4*
[b] *Nanox Inc., 4975 Rue Rideau, Que., Canada G2E 5H5*

Received 3 March 2006; received in revised form 12 June 2006; accepted 13 June 2006

Abstract

Perovskite-type materials $LaCoO_3$, $LaCo_{1-x}Cu_xO_{3-\delta}$, and $Cu_2O/LaCoO_3$ were synthesized by the mechano-synthesis process known as reactive grinding. Their characterization was performed by BET, X-ray diffraction, SEM, O_2-TPD, and H_2-TPR. The partial cobalt substitution by copper in perovskite lattice gives rise to a distorted structure of $LaCoO_3$ and influences the thermal stability and redox properties of perovskites. Temperature-programmed reduction (TPR) analysis showed a complete reduction of Co^{3+}, Cu^{2+} to metallic state in the temperature range of 310–580 °C. A lower cobalt reduction temperature observed for $LaCo_{1-x}Cu_xO_{3-\delta}$ in comparison to $LaCoO_3$ produces a finely dispersed bimetal on a La_2O_3 support. Quantitative TPR data showed that cobalt ions in the grain boundaries of the ground perovskites are directly reduced to metals at a relatively low temperature (310–450 °C). The existence of strong cobalt–copper interaction in perovskites could enhance the metallic dispersion of cobalt and prevent copper sintering. The reduced forms of $LaCo_{1-x}Cu_xO_{3-\delta}$ catalysts were tested as alcohol synthesis catalysts in a fixed bed flow reactor system at 275 °C and space velocity of $4000\ h^{-1}$ ($H_2/CO = 2/1$). A mixture of C_1–C_7 alcohols with the chain growth propagation factors of 0.34–0.42 was produced. The alcohol productivity is from 36.5 to 49.6 $mg/g_{cat}/h$ and selectivity towards higher alcohols took values in the range of 40–49.5%. The preliminary catalytic data indicated that copper located outside of the perovskite lattice is solely leading to the production of methanol and methane whereas its location in the octahedral position of the perovskite precursor framework is necessary for higher alcohol synthesis. Therefore, a uniform distribution of the metallic cobalt–copper atoms in the prereduced catalysts is crucial for the conversion of carbon monoxide and hydrogen into higher alcohols.

Keywords: Perovskites; $LaCoCuO_3$; High dispersion; Higher alcohols; Syngas; Co–Cu

---

1. Introduction

Mixtures of higher alcohols are known as interesting blend stocks for motor gasoline. The addition of oxygenates, such as alcohols and ethers, into gasoline gives rise to decreased toxic exhaust gases (CO, NO_x) and in some cases increased octane number. As a part of the Clean Air Act Amendments of 1990, the use of reformed gasoline requiring a minimum of 2.0% oxygenate has been mandated by the United States Congress to be used in cities with high level of air pollutants [1]. Therefore, the selective production of oxygenated compounds remains one of the main goals of syntheses from carbon monoxide and hydrogen. Methanol synthesis carried out over both low temperature and pressure (250 °C, 750–1000 psi, $Cu/ZnO/M_2O_3$, M = Al, Cr) and high temperature and pressure (400 °C, 1500–3000 psi, ZnO/Cr_2O_3) from syngas is a large scale industrial process [2–4]. Based on these catalysts, several other processes are under investigation. Among those, the synthesis of higher alcohols has been performed over both low- and high-temperature catalysts doped with alkali metal ions in order to shift the synthesis away from methanol towards higher alcohols [4–9]. Modified Fischer–Tropsch [3], group VIII metal-based catalysts [10,11] and developed Mo-catalysts [12] have been extensively investigated in catalysis for the development of active and selective alcohol synthesis catalysts. The catalysts based on Co–Cu reported by IFP (Institut Français du Pétrole) showed high activity and good selectivity toward higher alcohols [13]. These catalysts were such that neighboring cobalt and copper ions in the spinel structure remaining at atomic distance from each other in the reduced catalyst constituted the active center for the alcohol synthesis [13]. It is thus likely that using other mixed oxides comprising both Co and Cu may be interesting catalyst precursors.

Traditional ABO_3 perovskite-type mixed oxides have been known as catalysts or catalyst precursors for several oxidation/reduction reactions [14,15]. A large number of natural and synthetic compounds have the perovskite structure in which the

---

[*] Corresponding author. Tel.: +1 418 656 2708; fax: +1 418 656 3810.
E-mail address: Serge.Kaliaguine@gch.ulaval.ca (S. Kaliaguine).

0926-860X/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.apcata.2006.06.029

A and B positions can be occupied by a broad range of metal cations in different oxidation states [16]. The ideal perovskite structure is cubic with space group $Pm3m\text{-}O_h$ [16–18]; distortions owing to ionic size requirements of the structure can, however, give rise to modified structures, usually by tilting or twisting of the octahedra [19]. Such distortions make larger unit cells and accommodate reduction in symmetry. The crystal structure of perovskite materials is very tolerant to changes in the radii of A and B cations and could accommodate a large concentration in cation vacancies particularly at the A site. This allows a great flexibility in mixing A and B cations to obtain several desired physical chemical properties [16,18,20,21]. The large variety of properties displayed by perovskite oxides is due to the ability of the framework to accommodate cations of various sizes and valences and to tolerance towards anionic and cationic vacancies. In general, the catalytic activity of perovskite compounds is essentially controlled by the B-site metal, the effect of rare earth ion in the A site is usually meager [14,16,17,22]. Moreover, complex perovskites where both A and B sites are replaced by other elements in order to produce numerous derivatives of $AA'BB'O_3$ type have received much attention in catalysis [17,20,21,23]. The effect of a partial substitution of the B cation $(AB_{1-x}B'_xO_3)$ on the catalytic properties has been much less investigated because of difficulties in preparing the complex perovskites from elements with different radius and valence. For instance, Porta et al. [23] reported that the presence of a single perovskite phase of $LaCo_{1-x}Cu_xO_3$ was solely obtained at relatively high calcination temperature (≥800 °C) with $x < 0.4$. At higher concentration of copper ($x \geq 0.4$), the appearance of $LaCu_2O_4$ phase in addition to the $LaCo_{1-x}Cu_xO_3$ perovskite could not be avoided. Nevertheless, these perovskites do exhibit several interesting features as precursors for supported metal catalysts. For instance, the reduction under controlled reduction treatments of $LnBO_3$ (B = Mn, Ni, Co, Fe, Rh, ...) can produce a well-dispersed transition metal B on a matrix comprising a Ln_2O_3 support. Such catalysts were paid much attention for water gas shift reaction, partial oxidation of methane [14], reforming of carbon dioxide [24], alkene hydrogenation, alkane hydrogenolysis, [25], and Fischer–Tropsch synthesis [26], as well as higher alcohol synthesis [10,27]. However, the applications of these perovskite-type oxides as catalysts or catalyst precursors are limited due to the difficulties in obtaining high surface area owing to the high calcination temperatures during their preparation. It should be kept in mind that the preparative recipe plays an important role in the physical and chemical properties of the reaction products, governing the structure, morphology, and surface area of the obtained materials [18,19,27–31]. Compared to the conventional methods, reactive grinding allows to prepare perovskite-type mixed oxides at rather low temperatures and yields a relatively high surface area [28,30–32]. In previous publications [31,33–36], we presented a series of perovskites prepared by mechano-synthesis from their corresponding component oxides and their catalytic activity in various oxidation reactions. This article provides several further characterizations and reports a novel applicability of reactive $LaCoO_3$ perovskites partially substituted by copper as catalyst precursors for the synthesis of hydrocarbons and higher alcohols from syngas.

2. Experimental

2.1. Preparation of catalysts

A series of $LaCo_{1-x}Cu_xO_{3-\delta}$ ($0 \leq x \leq 0.6$) perovskite-type mixed oxides was synthesized by high-energy ball milling directly from the oxide precursors. Commercial lanthanum, copper, and cobalt oxides with purity of 99% or better, obtained from Aldrich, were weighed in stoichiometric proportions and blended together. A typical charge of 5 g blended raw materials together with three hardened steel balls of 11 mm in diameter were charged in a 50 ml hardened steel crucible. Then, the crucible was closed under air and fixed on the mill arm. An O-ring was placed between the crucible and the screw cap in order to keep the crucible hermetically sealed. A SPEX high-energy ball mill operating at 1000 rpm was used for mechano-synthesis. Milling was carried out for 8 h prior to a second milling step with additives. In the second milling step, the resulting powder was mixed to 50% NaCl (99.9%) and milled under the same conditions in order to reach a better dispersion and higher specific surface area. The secondary milling was carried out for 12 h before washing the NaCl additive with distilled water. Two leaching operations were performed in order to remove the additive. The slurry was then dried and calcined at the desired temperature. The $LaCo_{1-x}Cu_xO_{3-\delta}$ samples prepared by reactive grinding are designated below as N0–N6 (Table 1).

A reference sample, $LaCoO_3$ + 5.0 wt.% Cu_2O designated as M1, was prepared by grinding a mixture of the ground

Table 1
Preparation of $La(CoCu)O_{3-\delta}$ perovskites

Sample		Calcination temperature (°C)	S_{BET} (m²/g)	Composition (wt.%)			
				Na^+	Co	Fe	Cu
N0	$LaCoO_3$	250	59.6	0.53	21.15	4.69	–
N1	$LaCo_{0.9}Cu_{0.1}O_3$	250	19.5	0.31	19.31	1.12	1.89
N2	$LaCo_{0.8}Cu_{0.2}O_3$	70	30.5	0.08	18.22	–	2.64
N3	$LaCo_{0.7}Cu_{0.3}O_3$	250	22.3	0.17	16.77	1.21	5.79
N5	$LaCo_{0.5}Cu_{0.5}O_3$	250	10.6	0.44	10.60	0.64	9.96
N6	$LaCo_{0.4}Cu_{0.6}O_3$	250	20.5	1.04	9.81	1.00	11.58
M1	$Cu_2O/LaCoO_3$	120	16.8	0.39	20.04	4.78	3.28