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ScienceDirect

Journal of Catalysis 254 (2008) 218–225

JOURNAL OF CATALYSIS

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A mechanistic study of the low-temperature conversion of carbon monoxide to carbon dioxide over a cobalt oxide catalyst

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Received 6 July 2007; revised 9 October 2007; accepted 1 January 2008

Abstract

A nanocrystalline cobalt oxide (Co_3O_4)-based catalyst formed by heating a basic cobalt(II) carbonate precursor in air at 250–300 °C has been shown to exhibit much greater catalytic activity than Co_3O_4 calcined at higher temperatures. In a highly exothermic reaction, the properly calcined catalyst rapidly oxidizes carbon monoxide to carbon dioxide at room temperature. X-ray diffraction, X-ray photoelectron spectrometry, Brunauer–Emmett–Teller surface area measurements, and two FT-IR techniques were used to investigate the mechanism of the CO oxidation reaction. Diffuse reflection (DR) infrared spectrometry of the catalyst was used to monitor the gases adsorbed on the catalyst surface. The observation of a CO band at 2006 cm^{-1} indicates that CO is adsorbed onto cobalt atoms in a low oxidation state. The highest catalytic activity appears to be achieved when a specific ratio of Co(II) to Co(III) is found on the surface and the particle size is small (i.e., the surface area is large). Poisoning of the catalyst is evidenced in the DR spectra by the geminal adsorption of two CO molecules onto a cobalt atom in a high oxidation state, giving rise to a doublet at $\sim$2180 cm^{-1}. A strong band at 2343 cm^{-1} indicates that CO_2 is physisorbed onto the catalyst when it is poisoned. A unique ultra-rapid scanning FT-IR spectrometer was used to measure the concentration of the CO_2 formed, as well as that of the unreacted CO within 5 ms after the gas was passed through the catalyst. The spectra indicate that CO_2 is formed in a vibrationally excited state.

Keywords: Cobalt oxide; Low-temperature oxidation; Cabon monoxide; Diffuse reflection; Infrared; Vibrationally excited product

1. Introduction

The exothermic oxidation of carbon monoxide to carbon dioxide over metal oxide catalysts such as Co_3O_4 has been known since the 1920s [1,2]; over the last decade, several studies have revealed details of the reaction. For example, it has been shown that calcination in the presence of oxygen (also described as preoxidation in the literature) yields a highly reactive catalyst for the room-temperature oxidation of carbon monoxide with observed light-off temperatures as low as 210 K [3,4]. These catalytic species are very sensitive to the presence of water that appears to block reactive sites [4,5]. Reaction of CO alone with these catalysts initially yields CO_2, but the rate of this reaction drops quickly, indicating that active surface sites are being depleted. In contrast, mixtures of CO and O_2 maintain good rates of CO oxidation, suggesting that O_2 can replenish the catalytic sites. Furthermore, Jansson showed that when $^{18}O_2$ is used in the calcination step, $C^{16}O^{18}O$ is formed along with negligibly small amounts of $C^{18}O_2$ [6]. It is assumed that ^{18}O either exchanges with surface ^{16}O sites or oxidizes the Co(II) sites that remain after synthesis of the catalyst. Infrared (IR) bands characteristic of carbonate species have been observed on reaction of the cobalt catalysts with CO_2, and CO_2 has been shown to have an inhibitory effect on catalysis. Reaction of $C^{16}O_2$ with an $^{18}O_2$ calcined catalyst gives rise to $C^{16}O^{18}O$, indicating that exchange of surface oxygen with CO_2 can take place [6].

Of particular relevance to the present paper is the fact that several workers have carried out infrared (IR) spectroscopic studies of the catalysts after exposure to CO, CO_2, and mixtures

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doi:10.1016/j.jcat.2008.01.001

of CO and O_2. For example, Lokhov et al. [7], Goodsel [8], Busca et al. [9], and Lin et al. [10] used Co_3O_4 catalyst materials that had been exposed to high vacuum in the final steps of catalyst preparation. Lokhov et al. [7] also examined the absorption of CO onto Co_3O_4 surfaces at 80 K and observed bands in the infrared spectrum at 2137–2141 and 2125 cm^{-1}. These bands were assigned to metal carbonyl complexes involving Co(III) centers, but we note that free CO trapped in photochemical matrices at the same temperature is known to have stretching frequencies of 2140–2130 cm^{-1}, depending on the matrix environment. Goodsel [8], Busca et al. [9], and Lin et al. [10] have reported carbonyl bands at ca. 2180, 2120, and 2070 cm^{-1} on Co_3O_4 surfaces. At 150 K, the band at 2180 cm^{-1} appeared first, with the other bands appearing as the temperature of the sample was raised to 300 K. Evacuation of the samples led to loss of the two higher-frequency bands. At room temperature and above, bands assigned to carbonate accompanied the appearance of the metal carbonyl bands. Carbonate bands were reported at 1545 and 1324 cm^{-1} by Busca et al. and Goodsel and at 1570 and 1333–1302 cm^{-1} regions by Lin et al. These bands did not exactly match the expected positions for free carbonate (1440 cm^{-1}), unidentate carbonate (1470–1450, 1380–1350, 1070–1050 cm^{-1}), or bidentate carbonate (1640–1590, 1290–1260, 1040–1020 cm^{-1}) and are presumably caused by breaking of the trigonal symmetry of free carbonate ions. The bands reported by Busca et al., Goodsel, and Lin et al. stand in sharp contrast to bands at ca. 1605, 1420, and 1220 cm^{-1} on preoxidized Co_3O_4 reported by Jansson et al. [11,12]. A pair of bands at 2155 and 2178 cm^{-1} that were assigned to cobalt carbonyl groups also was observed by Jansson et al.

A group of bands at 1300–990 cm^{-1} was assigned by Jansson to a surface O_2^{n-} species involving O_2 reactions with iron surfaces by analogy to earlier work of Al Mashta et al. [13]. These low-frequency bands, which were assigned to harmonics of skeletal bands, also were reported in the spectra of evacuated samples by Busca et al. Because these bands were observed in samples that had been heated to remove a nonstoichiometric excess of oxygen, Jansson's assignment of the bands at 1640–1200 cm^{-1} to cobalt carbonyl groups appears to be incorrect.

Finally, we note the work of Todorova et al. [14], who prepared cobalt oxide catalysts on alumina by the thermal decomposition of $Co(NO_3)_3$. Heating these materials to 573 K in a stream of hydrogen followed by exposure of the catalyst to CO resulted in the appearance of a band at 2170 cm^{-1} similar to the high-frequency bands noted above. When these catalysts were reduced by heating to 723 K in a stream of hydrogen and then exposed to CO, a new band at 2005 cm^{-1} was observed.

In this paper, we report the results of our investigation of the reaction mechanism of the room-temperature oxidation of carbon monoxide to carbon dioxide over a cobalt catalyst prepared by the calcination of basic cobalt(II) carbonate at temperatures significantly below 500 °C. When basic $CoCO_3$ is calcined in air at ~250 °C, it is largely decomposed to the oxide, and the Co(II) is partially oxidized to Co(III), to form what is nominally "Co_3O_4" but which shows signs of retaining some of its original carbonate content (see below), compared with samples prepared by calcination at much higher temperatures.

2. Experimental

2.1. Catalyst preparation

Basic $CoCO_3$ was synthesized by dissolving cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) in water and subsequent acidification with concentrated nitric acid (Ref. [15], Example 15). This solution was then added dropwise over several hours to a stirred solution of excess sodium carbonate. The resulting precipitate was vacuum-filtered and thoroughly washed with distilled water. The washed precipitate was dried at 110 °C in ambient air for 12 h to produce the basic $CoCO_3$ catalyst precursor. This catalyst precursor was crushed and sieved to form a fine powder, which was then heated in a tube furnace at ca. 250 °C with flowing nitrogen and 21% oxygen at a rate of 200 mL/min to form the cobalt oxide catalyst.

2.2. Catalyst characterization

The catalyst formation was investigated using thermogravimetric analysis (TGA) (Netzsch STA49PC). Approximately 5 mg of 20- to 40-mesh basic cobalt carbonate was placed in an aluminum sample pan. The catalyst was then calcined *in situ* by heating it to 250 °C at 20 °C/min, holding at this temperature for 1 h, and then cooling it to 30 °C, under a flow of 21% oxygen in helium (BOC Gases) at 200 mL/min. The weight loss of the sample was recorded during calcination. After calcination, the gas was switched to a carbon monoxide and oxygen mixture in helium (3.4% CO, 10% O_2 and 86.6% He; BOC Gases), again at 200 mL/min. This mixture was flowed over the catalyst for 2 h, during which time the heat generated by the exothermic reaction was recorded by differential scanning calorimetry (DSC). Values of the exotherm were recorded after 10 min of exposure and again after 2 h.

Elemental ratios of carbon, oxygen, and cobalt and the ratio of Co(II) to Co(III) in the catalyst were determined using X-ray photoelectron spectrometry (XPS). In this procedure, 50-mg samples of 20- to 40-mesh basic cobalt carbonate were calcined for 1 h at 200, 250, 300, or 400 °C. Subsamples of the calcined catalyst and the basic cobalt carbonate were pressed into indium and then loaded into a 10^{-9} Torr vacuum chamber for examination with a Kratos Axis 165 XPS (15 mA, 13,500 kV, MgK_α radiation source, 3-mm^2 focal point area, 0.8-eV resolution). Survey scans (0–1000 eV) were performed for determination of purity and elemental ratios, and detailed scans in the 770–815 eV region were run to determine the Co(II):Co(III) ratio using the cobalt $2p_{3/2}$ and $2p_{1/2}$ electron emission peaks. Gaussian peak fitting was performed using Shirley baseline correction.

The catalyst surface area was measured with a 5-point BET analysis with nitrogen at 77.4 K using a Quantachrome AUTOSORB-1 analyzer. Powder X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert system (45 kV, 40 mA, CuK_α radiation source).