

Short communication

Low-temperature efficient degradation of ethyl acetate catalyzed by lattice-doped CeO₂–CoO_x nanocomposites



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ABSTRACT

A series of CeO₂–CoO_x nanocatalysts have been synthesized by a facile surfactant-free hydrothermal method and investigated for the oxidative degradation of ethyl acetate (EA) at exceptionally low temperature. The combination of various techniques, such as H₂-TPR, XRD, XPS and HRTEM provides insights to the effect of various factors including redox properties, enhanced lattice oxygen and its mobility *etc.* on catalysis performance. The results demonstrate that the enriched lattice oxygen is the dominant factor for the low-temperature degradation of EA due to the interaction between lattice-mixed Ce and Co ions, which can be used to design the catalysts for removing VOCs with improved performance.

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1. Introduction

Volatile organic compounds (VOCs) are one of the most hazardous classes of organic pollutants. They are emitted from various anthropogenic activities and cause many environmental problems such as the formation of photochemical smog and the depletion of stratospheric ozone [1–4]. Ethyl acetate (EA) is one of the most common, ascendant and stable volatile organic solvents. Its long term exposure can cause severe health problem to human beings. This hazardous nature of EA urges the researchers to fabricate new materials and seek better approaches to its complete removal [5,6].

Catalytic combustion has been recognized as an efficient technology for EA degradation, where both noble and transition metals have been used as catalysts. However, transition metal oxides are more active for the oxidation of oxygenated VOCs besides their thermal stability and low cost, and are not prone to sintering and poisoning. Recently, CeO₂–CoO_x composites have attracted special attention in catalytic removal of numerous VOCs, which demonstrate higher catalytic activity than their individual components [7–12].

Although many works have been done previously, to develop a system to degrade EA at reduced temperature is still needed. Therefore, to elucidate the low-temperature catalytic activity of the CeO₂–Co₃O₄ composites towards the oxidative degradation of EA is the main aim

of this work. Herein, the difference in catalytic activities by varying molar ratios of Ce–Co is compared and evaluated, and the attention is also paid to analyze the interaction between CeO₂ and Co₃O₄ and the effect on its redox property, lattice oxygen storage and mobility.

2. Experimental

A facile surfactant-free hydrothermal method is used to prepare the catalysts and the detailed procedure is provided in Supporting Information (SI).

3. Results and discussion

3.1. Catalytic performance

Fig. 1a shows the degradation of EA over pure and composite oxides. The catalytic activity decreases in the order Ce_{0.5}Co_{0.5} > Ce_{0.7}Co_{0.3} > Ce_{0.3}Co_{0.7} > CeO₂ > Co₃O₄. The temperature of 50 and 90% of EA conversion, *T*₅₀ is 178, 184, 186, 189, and 218 °C while *T*₉₀ is 195, 208, 211, 215 and 244 °C respectively. All other catalysts display higher *T*₁₀₀ (total conversion) for EA oxidation than Ce_{0.5}Co_{0.5} (*T*₁₀₀ = 200 °C). The activity follows the same trend for these catalysts even at lower temperature. In addition, the superiority of Ce_{0.5}Co_{0.5} among all the catalysts is confirmed by calculating the reaction rate of the samples at 156 °C (EA conversion <20%) as shown in Table S1, where Ce_{0.5}Co_{0.5} shows the best catalytic performance that may be attributed to the stronger interaction between CeO₂ and Co₃O₄ due to the doping of Co₃O₄ in an appropriate ratio into

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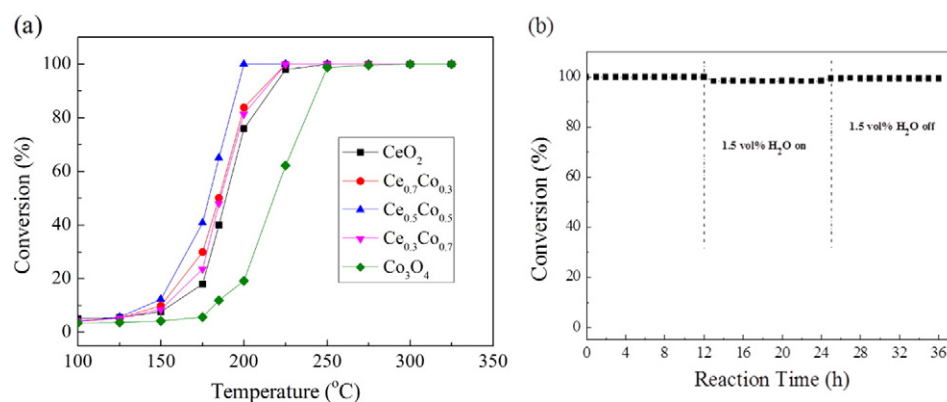


Fig. 1. Ethyl acetate conversion as a function of temperature over CeO₂, Co₃O₄ and Ce_xCo_{1-x} catalyst (a) and effect of moisture on catalytic performance of Ce_{0.5}Co_{0.5} catalyst at 200 °C (b).

CeO₂ lattice. This assumption will be further discussed in the following sections. In addition, the catalytic efficiency of the composite oxide is compared with other groups' works for the combustion of EA under similar conditions as shown in SI (Table S2).

Ce_{0.5}Co_{0.5} is used to investigate the effect of the moisture and space velocity on the oxidative degradation of EA due to its best performance among all catalysts. Fig. 1b demonstrates that the moisture has a negative effect on the catalysis. However, in the absence of moisture the catalytic performance recovers and remains constant for further 12 h. This inhibitory effect of the moisture indicates that the water molecules may compete with EA to adsorb on the surface of the catalyst during catalysis. In addition, the increase of the gas flow rate (Fig. S1) appears to be another negative effect on the catalytic performance which can be attributed to the shortened time of interaction between the catalyst and the VOC.

3.2. Catalyst characterization

The crystal phases are determined by XRD. Fig. 2a confirms that the catalysts possess fluorite phase of CeO₂ (JCPDS # 81-0792) and spinel structure of Co₃O₄ (JCPDS # 74-2120) respectively. The addition of Co to CeO₂ causes the change in the structural (Table S3) and textural properties of the final products (Table S4). The decreased lattice parameter suggests that Co³⁺ or Co²⁺ ions are incorporated into CeO₂ lattice to form a solid solution, since the effective ionic radius of Co³⁺ (0.065 nm)

or Co²⁺ (0.082 nm) is smaller than that of Ce⁴⁺ (0.111 nm), these findings are in a good agreement with the Raman analysis (Fig. S2 and S3). In addition, the characteristic peak of CeO₂ (111) at 28.6° gradually shifts towards the higher value as the cobalt content increases (Fig. 2b). The decreased lattice parameters of ceria are the evidence of solid solution formation [13]. However, the incorporation of cobalt ions in ceria framework leads to the formation of CeO₂-Co₃O₄ solid solution and the enhanced oxygen mobility due to increased oxygen vacancies [14] and will be discussed in the following paragraphs.

Fig. 3a shows that pure CeO₂ exhibits nanorod-like morphology while Ce_{0.5}Co_{0.5} composite oxide shows a mixture of nanorods and particles (Fig. 3b), where the nanoparticles are confirmed as Co₃O₄- and the nanorods are CeO₂-enriched phases as determined by HRTEM (Fig. 3e). Pure Co₃O₄ has hollow donut-like morphology (Fig. 3c). Lattice fringes (Fig. 3d) in HRTEM are 0.31 nm corresponding to the *d*(111) of CeO₂ and 0.46 nm assigned to (111) of Co₃O₄ (Fig. 3f). The EDS spectra of Ce_{0.5}Co_{0.5} composite oxide are provided in SI (Fig. S4). Typical HAADF images are displayed in Fig. 3g. Taking all these HAADF information into account, it can observe that both Ce and Co are homogeneously dispersed across the whole Ce_{0.5}Co_{0.5} catalyst, which is crucial for the enhanced oxygen storage and mobility, that in turn, affects the catalytic activity.

The oxidation state of catalyst surface species is examined by XPS analysis. Owing to the similarities in XPS patterns of all the samples, (Fig. S5) the pattern of Ce_{0.5}Co_{0.5} is chosen as the representative for

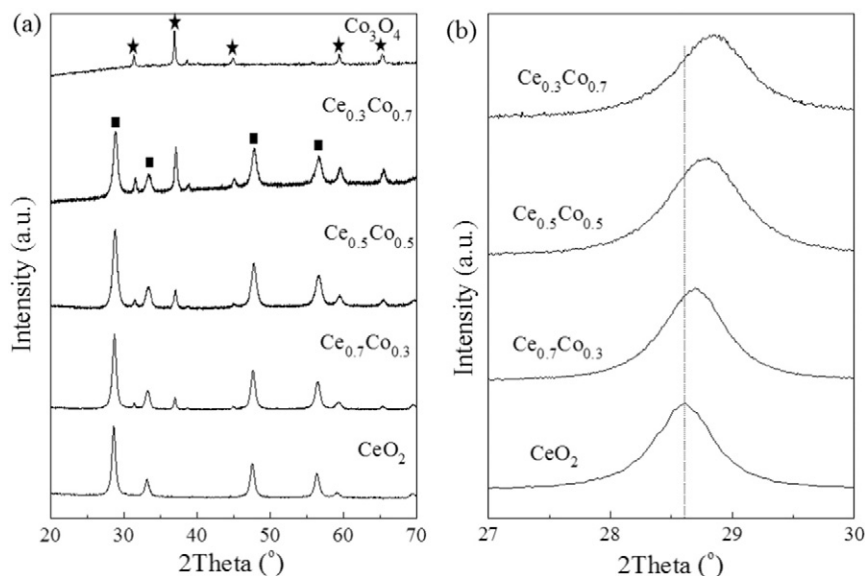


Fig. 2. XRD patterns of CeO₂, Co₃O₄ and Ce_xCo_{1-x} composite oxides: (a) wide angle patterns, and (b) enlarged zone patterns. Crystalline phases detected: Co₃O₄ (*) and CeO₂ (■).

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