Synergistic Effects of Co$_3$O$_4$-CeO$_2$ Nanoparticles towards Catalytic Oxidation of Aromatic Hydrocarbons: A Study in Association with Carbon Monoxide and Humidity

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In this study, a series of Co$_3$O$_4$-CeO$_2$ nanocomposites with various Co$_3$O$_4$ loading were fabricated by the impregnation method using cobalt(II) acetate as the cobalt precursor for the treatment of benzene, toluene, ethylbenzene, and xylene (BTEX). The as-prepared Co$_3$O$_4$-CeO$_2$ nanocomposites were thoroughly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), hydrogen temperature-programmed reduction (H$_2$-TPR), and temperature-programmed desorption (O$_2$-TPD). The excellent reproduction of active oxygen species caused by the high dispersion of Co$_3$O$_4$ crystals on the CeO$_2$ supports was established. In addition, the reduction peaks of Co$_3$O$_4$-CeO$_2$ nanocomposites were found at much lower temperatures compared to pure CeO$_2$, considering their unique redox property influencing the high catalytic activity. Among the characterized materials, the 5.0 wt.% Co$_3$O$_4$ supported on CeO$_2$ (5.0Co–Ce) was the best system for catalytic oxidation of xylene, along with excellent performances in the cases of benzene, ethylbenzene, and toluene. Its catalytic activity increased in the order: benzene < xylene < ethylbenzene < toluene. Furthermore, the addition of carbon monoxide (CO) as a coreactant permitted to improve the catalytic performances in such oxidations as well as the stability of as-prepared catalysts, even under humid conditions.

1. Introduction

Aromatic hydrocarbons involving benzene, toluene, ethylbenzene, and xylene (BTEX) are air pollutants, mainly found in oil deposits and natural gas, or petroleum refining and petrochemical plants [1, 2]. Many serious health threats (nausea, headache, and fatigue) can be posed by exposure to BTEX for a long time [3]. Therefore, the elimination of BTEX is urgent, normally based on chemical reaction with chemical reagents, adsorption process using porous materials, and catalytic oxidation with a heterogeneous catalyst. In particular, catalytic oxidation processes have been delighted as the most important and up-and-coming technologies, due to the simple operation of equipment, the high removal efficiency, producing nontoxic products involving CO$_2$ and H$_2$O [4].

Commonly, the composites of CoO$_x$-CeO$_2$ exhibited excellent catalytic performances in low-temperature volatile organic compounds oxidation [5], CO oxidation [6], and N$_2$O decomposition [7]. Synergistic effect of CoO$_x$ and CeO$_2$ on such processes has been illuminated, taking into account the oxygen mobility on the oxides surfaces and the oxygen storage capacity (OSC) of CeO$_2$ [8]. In comparison with expensive Pt-based catalysts, CoO$_x$ displayed the equivalent catalytic activity. Besides, supported-CoO$_x$ catalysts
have been favored than nonsupported ones as the results of their sintering resistance as well as higher activity [9]. Recent efforts focused on CeO$_2$ support considering its high OSC [10], oxygen mobility [11], and acidic features [12]. Besides, the metal-support synergy based on CeO$_2$ support results in the high dispersion of CoO$_x$ in their matrix.

The most frequently used method to synthesize CoO$_x$-CeO$_2$ composites is the aqueous impregnation of CeO$_2$ support in the aqueous solutions of cobalt salts. The metal site dispersion on CeO$_2$ determines both their activity and selectivity, prompting the development of synthetic methods based on different cobalt salts [13] involving cobalt(II) nitrate [14], cobalt(II) acetate [15], or organometallic cobalt-based complexes. Furthermore, the redox flexibility of CoO$_x$ provoked by Co(III)/Co(II) couple plays a significant factor in controlling their oxidation catalytic activity [9, 16]. The reducing feature could be varied depending on metal precursor types, promoters, and supports [17]. According to our previous study, the Co$_3$O$_4$/CeO$_2$ catalyst coming from cobalt(II) acetate gave an excellent performance for $p$-xylene oxidation [18]. As a part of catalyst characterization, the decrease of Co$_3$O$_4$ crystal size and the insertion of cobalt cations into CeO$_2$ lattice prompted increases of surface area and bulk lattice oxygen, as well as a drop of the reducing temperature. These features provided positive impacts on the remarkable catalytic performances of Co$_3$O$_4$-doped CeO$_2$.

Figure 1: XPS spectra of (a) Co 2p, (b) Ce 3d, and (c) O 1s for 5.0Co-Ce sample.
In the catalytic oxidation processes of volatile organic compounds (VOCs) and CO, water vapor (as an oxidation product or moisture in the gas) can influence on the reaction kinetics, leading to the interference on their reaction rate [19]. In fact, the surface OH\(^{-}\) groups can block active sites, as well as cutting off oxygen exchange at catalyst sites/support interfaces [20]. The surface OH\(^{-}\) groups formation was boosted by high concentrations of water vapor and oxygen [21]. Thus, the oxygen exchange capability of catalytic supports and the metal-support synergy should be governed with the aim of enhancing the VOC removal in the presence of water vapor. It was consistent with the abovementioned properties of CeO\(_2\) and the synergistic effects of the CoO\(_x\)-CeO\(_2\) mixed oxides.

In this study, the influences of cobalt contents on the physicochemical characteristics of CeO\(_2\) nanoparticles-supported Co\(_3\)O\(_4\) were investigated, shedding light on their catalytic activities towards the BTEX deep oxidation, in particular in the presence of CO and water vapor.

2. Results and Discussion

2.1. Catalyst Characteristics. Firstly, CeO\(_2\) nanoparticles coming from Ce(NO\(_3\))\(_3\).6H\(_2\)O were prepared by hydrothermal approach [22], and then, a series of Co\(_3\)O\(_4\) supported on CeO\(_2\) nanoparticles were fabricated by the impregnation technique using cobalt(II) acetate as the cobalt precursor (with the contents of 2.5, 5.0, 7.5 wt.% Co\(_3\)O\(_4\) symbolized as 2.5Co-Ce, 5.0Co-Ce, and 7.5Co-Ce), as previously reported by our group [18] (Experimental, in the Supplementary Information). The face-centered cubic crystalline structure of CeO\(_2\) was characterized by XRD analysis and even preserved after loading of Co\(_3\)O\(_4\) (Figure S1). However, the high dispersion of Co\(_3\)O\(_4\) on the support interfered with the observation of their crystals for all the samples [12]. The oxidation states of the sample of 5.0 wt.% of Co\(_3\)O\(_4\) supported on CeO\(_2\) (5.0Co-Ce) were studied by XPS analysis (Figure 1) by reason of the highest catalytic activity (see the next section). A major peak of Co 2p3/2 was detected at 779.7 eV binding energy (Figure 1(a)) [23], and the corresponding Co\(^{2+}\)/Co\(^{3+}\) ratio in the sample was estimated at 2.54. The Ce\(_{3}\)d XPS spectra of the 5.0Co-Ce sample (Figure 1(b)) show the exclusive presence of Ce\(^{4+}\) species with six peaks at 881.7 eV (\(\alpha\)), 888.3 eV (\(\beta\)), 897.6 eV (\(\gamma\)), 900.5 eV (\(\alpha'\)), 907.2 eV (\(\beta'\)) and 916.4 eV (\(\gamma'\)) [24]. In fact, the high binding energy (BE) doublet \(\alpha'/\beta'\) corresponds to Ce(IV) 3d\(^{4}\)F\(_{2}\)2p\(^{1}\), doublet \(\beta/\beta'\) is originated from Ce(IV) 3d\(^{4}\)F\(_{2}\)2p\(^{0}\), and doublet (\(\gamma/\gamma'\)) is associated to Ce(IV) 3d\(^{4}\)F\(_{0}\)2p\(^{2}\), whereas no Ce\(^{3+}\) species was detected [25].

The O 1s spectra of the 5.0Co-Ce sample (Figure 1(c)) show the peaks at medium (531.3 eV) and high (528.9 eV) binding energies indicating adsorbed surface oxygen (O\(^{2-}\), O\(^{−}\), O\(^{2−}\)) and lattice (O\(^{2−}\)), respectively. A broad peak (533.3 eV) was observed due to the presence of the defective oxides or hydroxylated surface of the 5Co-Ce sample. This property confirmed the improvement of oxygen storage capacity and mobility provoked by the strong synergy between CeO\(_2\) and Co\(_3\)O\(_4\) [26].

The adsorption-desorption isotherms (Figure 2) revealed that both CoO\(_x\)-doped and undoped CeO\(_2\) nanorods obey type IV isotherms (hysteresis loops at relative pressures greater than 0.5), confirming their mesoporous structures [27, 28]. The Barrett-Joyner-Hallenda (BJH) pore size distributions of ceria and Co-Ce samples (Figure 2) indicated their maximum pore diameters (more than 10 nm), in agreement with the mesopores of the samples. As clearly, the addition of cobalt in CeO\(_2\) did not affect their pore size distributions.

The undoped ceria sample (Ce) exhibited a BET value of 43.3 m\(^2\) g\(^{-1}\), an average pore diameter of 23.8 Å, and a pore volume of 0.057 cm\(^3\) g\(^{-1}\). The addition of CoO\(_x\) from 2.5 wt.% to 5.0 wt.% led to increasing the surface area of composites (48.5-51.0 m\(^2\) g\(^{-1}\)) but decreasing applying the higher CoO\(_x\) loading (7.5 wt.% and 37.6 m\(^2\) g\(^{-1}\)) (Figure 3), being consistent with the previous study [29]. The high surface area of Co-Ce composites may affect the BTEX oxidation activity, which depends on the number of active sites. The similarity was inspected for their pore volumes (see in Figure 4); meanwhile, the average pore diameters slightly decreased as adding CoO\(_x\) to ceria (23.0-23.6 Å).

The morphology of samples (Figure S2) show that pure CeO\(_2\) composed of homogeneous particles has a bigger size. CeO\(_2\) crystals were highly minimized by CoO\(_x\) addition, particularly on the 5.0Co-Ce sample. In the Co-Ce samples, the highly dispersed CeO\(_2\) could resist the sintering of CoO\(_x\) and thus improve their thermal stability [30]. Thus, the suitable content of CoO\(_x\) in the 5.0Co-Ce sample could increase its surface area. The microstructural characteristics of the 5.0Co-Ce sample were observed by HR-TEM analysis (Figure 5). The CeO\(_2\) nanoparticles were 20-30 nm in diameter (being consistent with the previous SEM analysis), with (111), (200), and (220) crystal planes corresponding to the d-spacings of 0.27, 0.25, and 0.27 nm. Furthermore, CoO\(_x\) nanocubes (the range size of 10-15 nm) were dispersed on CeO\(_2\) nanoparticles, with the d-spacings of 0.15 and 0.16 nm assigned to (220) and (111) crystal planes of the CoO\(_x\) phase.

The FT-IR spectrum of CeO\(_2\) exhibited the presence of absorption bands at 450 cm\(^{-1}\), 1630 cm\(^{-1}\), and 3430 cm\(^{-1}\)
attributed to CeO$_2$ stretching, the molecular H$_2$O bending [31], and the O-H stretching vibrations of hydroxyl functional groups [32], respectively (Figure 6). The absorption characteristics were not different after loading Co$_3$O$_4$ on CeO$_2$. However, the FT-IR spectra of Co$_3$O$_4$-CeO$_2$ nanocomposites showed the higher signal intensities, proving that CoO$_x$ crystals are inserted into CeO$_2$ lattice and highly dispersed on CeO$_2$ supports. In particular, the 5.0Co-Ce sample showed the highest peak intensity and thus the superior catalytic activity in BTEX deep oxidation (see the next section).

The O$_2$-TPD profiles of xCo-Ce samples (Figure 7) indicated the oxygen desorption bands attributed to different oxygen species: surface-active oxygen (<350°C), surface lattice oxygen (350-500°C), and bulk phase lattice oxygen (>500°C) [33]. With the undoped CeO$_2$, two desorption peaks of surface adsorbed oxygen species at low temperatures (<350°C) were detected. Meanwhile, when Co$_3$O$_4$ was added to CeO$_2$ (2.5-5.0 wt.%), the more oxygen desorption peaks appeared and shifted to higher temperatures, indicating an obvious growth of O$_2$ adsorption capacity. By the increase of Co$_3$O$_4$ concentration (7.5 wt.%), the area of the peaks decreased, pointing out the difficulties in producing surface-active oxygen applying the higher CoO$_x$ contents. In this study, the 5.0Co-Ce catalyst gave the highest surface-active oxygen production, suggesting the better O$_2$ adsorption [34], being essential for their remarkable catalytic activity in BTEX deep oxidation.

The H$_2$-TPR profile of CeO$_2$ (Figure 8) displayed the weak and broad peaks at 400°C and 800°C, representing the reductions of surface and subsurface oxygen of ceria, respectively. On the Co-Ce nanocomposites, three reduction bands were detected at much lower temperatures with higher intensities in comparison with the pure ceria. The first peak at 200-320°C was contributed by the reduction from Co$_3^+$ to Co$_2^+$ and/or Co$_2^+$ to Co$_0$, the second peak with low intensity at 350-450°C was attributed to characteristic for Co$_3$O$_4$ bounded to CeO$_2$, and the third broad peak at 750-850°C was associated to the reduction of ceria subsurface oxygen [6, 35]. The ceria reducibility was enhanced with the assistance of Co$_3$O$_4$, because of a hydrogen spillover from cobalt to ceria. In which, the 5.0Co-Ce sample showed the highest reduction peaks at lower temperature range, accordingly being more easily reduced and the highest consumption of hydrogen. The results evidenced that the well-dispersed CeO$_2$ across the Co-Ce nanocomposites boosted the synergistic effect between CeO$_2$ and Co$_3$O$_4$, facilitating the active oxygen reproduction and thus improving the catalytic activity.
2.2 Catalytic Activity. Effect of cobalt contents on the catalytic activity in \( p \)-xylene oxidation (Figure 9) showed that the low conversions were achieved using the pure \( \text{CeO}_2 \) catalyst in the temperature range from 225 to 300 °C (59.7% conversion at 300 °C). On the other hand, the cobalt addition into the catalytic systems tremendously improved the catalytic performance. For all \( \text{Co-Ce} \) samples, the higher the reaction temperatures were, the higher the \( p \)-xylene conversions were. Generally, they reached over 85% conversions at 285 °C and the 5.0Co-Ce sample was the most efficient (92.6% conversion at 285 °C). These results are quite consistent with the previous catalyst characterization of the 5.0Co-Ce sample (5.0 wt.% \( \text{Co}_3\text{O}_4 \)) involving the smallest particle size, remarkable specific surface area, the most easily reduced catalyst, and the highest strength of the bonds on the surface.

The catalytic activity of the best system (5.0Co-Ce) in BTEX oxidation (Figure 10) indicated the increase of its catalytic activity following the order: benzene < \( p \)-xylene < ethylbenzene < toluene. In fact, the treatment efficiency of
aromatic compounds mainly depends on the adsorption strength of aromatic hydrocarbons, the C-H strength, and the ionization potential of methyl derivatives. In which, it reached 100, 98, 92, and 75% conversions corresponding to toluene, ethylbenzene, \( p \)-xylene, and benzene at 285°C. Balzer and coworkers reported \( \text{Co}_2\text{O}_4 \) (20 wt.%) catalysts supported on \( \text{CeO}_2 + \gamma\text{-Al}_2\text{O}_3 \) towards VOC oxidation involving \( n \)-hexane (96% conversion), benzene (90% conversion), toluene (70% conversion), and \( o \)-xylene (58% conversion) at 350°C [36]. Meanwhile, 20 wt.% \( \text{Co}_2\text{O}_4 + \gamma\text{-Al}_2\text{O}_3 \)-undoped \( \text{CeO}_2 \) achieved only 50%, 45%, 35%, and 25% conversions under the similar conditions. Wu and coworkers synthesized supported Au catalyst (1.5 wt.%) applied in \( p \)-xylene oxidation \[37\], reaching 30%, 14%, and 9% conversions at 300°C on \( \text{Au/ZnO}, \text{Au/Al}_2\text{O}_3, \) and \( \text{Au/MgO} \) catalysts, respectively. In comparison to the catalytic activities as above-mentioned, the 5.0Co-Ce catalyst gave a better catalytic performance, rising the efficient catalytic systems towards the BTEX oxidation.

The catalytic performances of the 5.0Co-Ce sample for \( p \)-xylene in the absence and presence of CO, the single CO oxidation are shown in Figure 11. The complete CO conversion in both cases was below 275°C. In the assistance of CO, an increase of the catalytic performance in \( p \)-xylene oxidation was observed. The exothermicity of the CO oxidation was
the cause of enhanced activity (enthalpy of the reaction of CO oxidation: $\Delta H = -282 \text{kJ mol}^{-1}$) [38]. The oxidation of CO to CO$_2$ was completed when $p$-xylene oxidation began. The CO oxidation can locally raise the temperature of the catalyst bed and permit to activate the $p$-xylene oxidation.

The stability of the 5Co-Ce sample in the $p$-xylene oxidation was examined in the presence of water vapor (Figure 12). Clearly, in the case of CO and water vapor, the $p$-xylene conversion remained stable after 360 minutes ($X_{p$-xylene} = 89 – 91\%) with various contents of water vapor (1.1-3.2 mol%). Meanwhile, without CO, the $p$-xylene conversion decreased applying the increase of water vapor concentration (82.4% conversion without water vapor vs. 59.1% conversion in the case of steam rising to 3.2 mol% at 275°C for 360 mins). However, when the water vapor was turned off, the xylene conversion increased significantly, from 59.1% to 78.5% in 480 mins. These results proved that the adsorbed steam only competes with the reactants, leading to inhibiting the catalytic activity but not poisoning the catalytic sites. In fact, the Co-Ce catalyst system is still highly durable upon the time, proving that the addition of CO in $p$-xylene vapor enhances both catalytic reactivity and stability.

3. Conclusion

The CoO$_x$-CeO$_2$ nanocomposites showed better catalytic activity in the BTEX oxidation reaction compared to the pure CeO$_2$. The phase synergy between CoO$_x$ and CeO$_2$ contributed to their activity improvement. The 5.0Co-Ce sample exhibited the highest catalytic performance towards BTEX oxidation, reaching 100% (toluene), 98% (ethylbenzene), 92% ($p$-xylene), and 75% (benzene) conversions at 285°C. In contrast, the pure CeO$_2$ showed a low $p$-xylene conversion (43.5% at 285°C). The presence of CO improved $p$-xylene oxidation on the 5Co-Ce catalyst owing to the exothermicity from CO oxidation, increasing the temperature of the catalyst bed, and thus activating the $p$-xylene oxidation. Besides, the catalyst stability upon the time in such a reaction was evidenced by the addition of CO, in the assistance of water vapor. This research demonstrated the catalytic efficiency of cobalt-doped ceria nanoparticles in aromatic hydrocarbons oxidations in association with CO and humidity.

Data Availability

The experimental data used to support the findings are included as the supplementary data within the article.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Supplementary Materials

Figure S1: XRD patterns of xCo-Ce samples. Figure S2: SEM images of samples. (a) Ce. (b) 2.5Co-Ce. (c) 5.0Co-Ce. (d) 7.5Co-Ce. (Supplementary Materials)


