Catalytic Liquid-Phase Oxidation of Phenolic Compounds Using Ceria-Zirconia Based Catalysts

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Catalytic liquid-phase oxidation using a catalyst and oxygen gas (Catalytic wet air oxidation, CWAO) is one of the most promising technology to remove hazardous organic compounds in wastewater. Up to now, various heterogeneous catalysts have been reported for phenolic compounds decomposition. The CeO$_2$-ZrO$_2$ based catalysts have been recently studied, because CeO$_2$-ZrO$_2$ works as a promoter which supplies active oxygen species from inside the lattice to the active sites. Since it is difficult to dissolve oxygen gas into water, the use of the promoter is effective for realizing the high catalytic activity at moderate conditions. Also, CeO$_2$-ZrO$_2$ shows high resistance for the metal leaching during the catalytic reaction in the liquid-phase. This article reviews the studies of the catalytic liquid-phase oxidation of phenolic compounds using CeO$_2$-ZrO$_2$ based catalysts.

Keywords: catalyst, liquid-phase oxidation, phenolic compounds, ceria-zirconia, catalytic wet air oxidation

INTRODUCTION

To date, industrial sector has been rapidly growing and consequently contributing to an increase in hazardous waste. Phenolic compounds, e.g., phenol, chlorophenol, and bisphenol-A, are well-known organic pollutants encountered in the wastewater. They have been used as raw material in many kinds of industries for the production, such as phenol resins, polycarbonate plastics, and acetylsalicylic acid. However, phenolic compounds are toxic substances for human health and lethal to aquatic life in water. Especially, bisphenol-A has identified as an endocrine-disrupting chemical (EDC) and functions as an estrogenic substance in living organisms even at very low concentration level (Geens et al., 2012). To protect the environment and our health, it is necessary to remove these pollutants from wastewater.

The conventional treatments are activated carbon treatment, coagulating sedimentation process, and biodegradation process (Chung et al., 2003; Villegas et al., 2016; Karri et al., 2017); however, these processes have problems, such as replacement of activated carbon, post-treatment of sediments, and control of temperature and pH for microorganisms. Although advanced treatment technologies have been studied using UV irradiation, strong oxidizing agents (H$_2$O$_2$ or O$_3$), Fenton reagent (H$_2$O$_2$ + Fe$^{2+}$), and ultrasound (Rosenfeldt and Linden, 2004; Torres et al., 2008; Nidheesh, 2015; Zhang et al., 2018), they require constant supply of hazardous oxidizing additives, UV irradiation, or ultrasonic irradiation.

A liquid-phase oxidation with a gaseous oxygen, wet air oxidation (WAO), is the simple process for wastewater treatment without photoirradiation, sonication, nor addition of oxidizing agent. However, the effective removal requires elevated temperatures (125–320°C) and high pressures...
(0.5–20 MPa) in order to increase the solubility of oxygen molecule in the solution (Zimmermann, 1958; Li et al., 1991; Mishra et al., 1995). One of the most promising processes to realize the high efficiency under the mild conditions is a catalytic liquid-phase oxidation, generally denoted as catalytic wet air oxidation (CWAO). Homogeneous catalysts based on copper salts are reported to exhibit effective catalytic oxidation for treating wastewater (Imamura et al., 1985, 1987; Ma et al., 2017), while these catalysts were deactivated because of the leaching of the active phase and the formation of carbonaceous deposits, likely due to the presence of manganese (Delgado et al., 2006). Noble metals (Pt, Ru, and Pd) have generally high catalytic activity and high resistance for metal leaching compared to metal oxides (Imamura et al., 1988; Masende et al., 2005). However, they still require severe reaction conditions compared to ambient temperature and pressure. Since it is difficult to dissolve oxygen gas into water at moderate conditions, a promoter which supplies active oxygen species from its lattice toward an activator is an important component. Recently, ceria-zirconia (CeO$_2$-ZrO$_2$) based catalysts have been paid attention for the wastewater treatment due to their high oxygen release and storage abilities.

In this mini-review, we provided the studies on the heterogeneous catalysts based on CeO$_2$-ZrO$_2$ solid solutions for catalytic liquid-phase oxidation of phenolic compounds.

**CeO$_2$-ZrO$_2$ SOLID SOLUTIONS**

CeO$_2$ is one of the most famous promoters, because of its unique non-stoichiometric characteristics resulting from the ability of easily transition between reduced and oxidized states (Ce$^{4+}$ ↔ Ce$^{3+}$ + e$^-$) (Trovarrelli, 1996; Montini et al., 2016). This allows CeO$_2$ to store gaseous oxygen into its crystal lattice and subsequently release active oxygen from the bulk material. Therefore, CeO$_2$ can work as a promoter to facilitate the oxidation of organic compounds by supplying active oxygen to the activator. Zirconium ions (Zr$^{4+}$) are generally introduced into the CeO$_2$ lattice to increase the oxygen release and storage abilities (Fornasiero et al., 1995). In the CeO$_2$-ZrO$_2$ binary system, various crystal structure have been reported. Yashima et al. proposed the phase diagram of the CeO$_2$-ZrO$_2$ system by using X-ray powder diffraction measurement and Raman spectroscopy (Yashima et al., 1994, 1995a; Vareš et al., 2006; Montini et al., 2016). The phase diagram shows three different tetragonal phases ($t$, $t'$, and $t''$), in addition to the monoclinic ZrO$_2$ phase and the cubic CeO$_2$ phase. The monoclinic and/or t phases were formed for CeO$_2$ content less than ca. 20 mol%, where the monoclinic phase is thermodynamically stable for pure ZrO$_2$ at room temperature. In the CeO$_2$ rich area above 90 mol%, the cubic phase was detected. The $t'$ and $t''$ phases were regarded as the metastable phase at intermediate compositions of 20–90 mol% CeO$_2$. For the 50 mol% CeO$_2$ content, other metastable structure has been identified to be pyrochlore, $κ$ and $t''$ phases, which are cation-ordered phases (Montini et al., 2016). According to Fornasiero et al. (1995), the highest oxygen storage value is found for the Rh supported on cubic Ce$_{0.5}$Zr$_{0.5}$O$_2$ sample. By applying the oxygen release and storage abilities, the CeO$_2$-ZrO$_2$ solid solution has been commercialized as promoters in automotive exhaust catalysts.

**CATALYTIC LIQUID-PHASE OXIDATION OF PHENOL**

As described in the Introduction section, phenol has received attention due to its toxicity and common pollutant in wastewater. In addition, since phenol is the simplest class among phenolic compounds, phenol is considered to be an intermediate in the catalytic oxidation of phenolic compounds. Therefore, phenol is generally selected as a model compound for the wastewater treatment using heterogeneous catalysts.

For catalytic phenol oxidation, noble metal loaded catalysts have been extensively studied due to their high catalytic activity and high resistance for the metal leaching. As for the noble metal activator, Barbier et al. (2005) investigated the Ru, Pd, or Pt supported on CeO$_2$ catalysts, and confirmed that the order of phenol conversion was: Ru > Pd > Pt. For the Pd activator, the abrupt deactivation was also observed due to the deposition of carbonaceous species. Lee et al. (2010) studied the deactivation of catalyst during the phenol oxidation, and demonstrated that the deactivation was accelerated especially for Pt/Al$_2$O$_3$ compared to Pt/CeO$_2$. They discussed that CeO$_2$ might have promoted the oxidation of the carbonaceous deposits on the catalyst. According to Nousir et al. (2008), when introducing ZrO$_2$ into the CeO$_2$ lattice, oxygen storage capacity (OSC) of Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ was significantly enhanced compared to that of Pt/CeO$_2$, indicating an increase in the oxygen species mobility. Although the phenol conversion of Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ (92%) was comparable with that of Pt/CeO$_2$ (94%) after the reaction at 160°C and 2 MPa for 3 h, the selectivity in the complete oxidation product (CO$_2$) for Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ (68%) was higher than that for Pt/CeO$_2$ (50%); i.e., the formation of carbonaceous species on Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ was suppressed compared to the Pt/CeO$_2$ case.

Based on the results mentioned above, the catalytic liquid-phase oxidation activities of phenol over the CeO$_2$-ZrO$_2$ based catalysts are tabulated in Table 1. Nousir et al. (2008) also compared the Pt/Ce$_{1-x}$Zr$_x$O$_2$ ($x = 0.9, 0.75, 0.5$) catalysts, and demonstrated that the phenol conversion was: Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ (92%) > Pt/Ce$_{0.5}$Zr$_{0.5}$O$_2$ (80%) > Pt/Ce$_{0.75}$Zr$_{0.25}$O$_2$ (67%), and the CO$_2$ selectivity was: Pt/Ce$_{0.9}$Zr$_{0.1}$O$_2$ (71%) > Pt/Ce$_{0.5}$Zr$_{0.5}$O$_2$ (61%) > Pt/Ce$_{0.75}$Zr$_{0.25}$O$_2$ (53%). Among them, the Pt/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst exhibited the highest OSC.
value, which caused the high CO₂ selectivity due to an easier elimination of the surface carbonaceous deposits. In addition, they assumed that the selectivity was also affected by the large interface between Pt and the support for Pt/CeO₂-ZrO₂. Keav et al. (2014) reported that Ru supported on ZrO₂-CeO₂O₂ showed the higher phenol conversion (ca. 97%) than the Pt supported case (ca. 92%) after the reaction at 160°C and 2 MPa for 3 h, similar to the pure ceria supported catalysts (Barbier et al., 2005). They also demonstrated that Zr₁₀(Ce₀.⁷₅Pt₀.₂₅)₉O₂ exhibited the high OSC value compared to Zr₀.₁Ce₀.₉O₂, because two kinds of valence states (Pt⁴⁺ and Pt⁶⁺) modified the kinetics of oxygen transfer, leading to promoting the redox process. However, the phenol conversions using Pt or Ru supported on Zr₀.₁(Ce₀.⁷₅Pt₀.₂₅)₉O₂ was lower than each catalyst without Pr ion (Table 1), due to the formation of carbonaceous deposits.

One possible reason of the low activity was the reduction treatment using hydrogen gas (30 mL·min⁻¹) at 350–800°C for 3 h before the catalytic phenol oxidation. According to Wang et al. (2008), a complete removal of phenol was realized for a Ru/ZrO₂-CeO₂ (Ce/Zr = 9) catalyst in the fixed-bed flow reactor by applying conditions of 4 MPa and 140°C. In a recent study, the effective phenol removal was demonstrated even at the moderate conditions by using the catalyst, which consists of Pt and Ce₀.₆₈Zr₀.₁₇Sn₀.₁₅O₂ dispersed on mesoporous silica SBA-16 (Santa Barbara Amorphous No. 16) with large surface area (Supandi et al., 2017). They reported that the phenol conversion of Pt/Ce₀.₆₈Zr₀.₁₇Sn₀.₁₅O₂/SBA-16 reached up to 91% after the reaction at moderate temperature of 80°C and the atmospheric pressure for 6 h. Here, only ca. 4% of phenol was adsorbed into the SBA-16 support, indicating that the catalytic reaction was proceeded. They also revealed that the conversion of Pt/Ce₀.₆₈Zr₀.₁₇Sn₀.₁₅O₂/SBA-16 was also higher than that of Pt/Ce₀.₈Zr₀.₂O₂/SBA-16 (85%). Based on the literature (Yasuda et al., 2012), the introduction of SnO₂ into the CeO₂-ZrO₂ lattice enhanced the oxygen release and storage abilities, because of the synergistically redox reaction between Ce⁴⁺/³⁺ and Sn⁴⁺/²⁺.

Noble-metal free catalysts for phenol removal have been also studied, as listed in Table 1. Delgado et al. (2012) investigated the catalytic activity of CeO₂-ZrO₂ without activators. Compared to pure CeO₂, Ce₀.₆₈Zr₀.₃₂O₂ showed the high performance, where the phenol conversions of CeO₂ and Ce₀.₆₈Zr₀.₃₂O₂ were 88.4 and 98.2%, respectively, after the reaction at 160°C and 2 MPa for 7 h. The enhancement in the activity was explained by the increase in oxide ion mobility; i.e., the vacancies or structural defects might form by the incorporation of Zr⁴⁺ into the fluorite CeO₂ structure. In the case of the Zr-rich sample (Ce₀.₁₅Zr₀.₈₅O₂), the activity decreased to 89.6% due to the segregation of ZrO₂. They also reported that a carbonaceous deposit was not observed after the reaction at 160°C, while the deposit covered the catalyst surface in the case of the reaction at 120°C, resulting the deactivation (phenol conversion of Ce₀.₆₈Zr₀.₃₂O₂: 60.9%). In addition, they revealed the high resistance for metal leaching of Ce₂O₃-ZrO₂ after the reaction.

Kim et al. (2009) developed various CeO₂-ZrO₂ supported metal oxide activators, and demonstrated that CuO/Ce₀.₆₅Zr₀.₃₅O₂ showed the high catalytic activity for phenol oxidation compared to MnOₓ/Ce₀.₆₅Zr₀.₃₅O₂, Fe₂O₃/Ce₀.₆₅Zr₀.₃₅O₂, CoOₓ/Ce₀.₆₅Zr₀.₃₅O₂, and NiOₓ/Ce₀.₆₅Zr₀.₃₅O₂. The complete phenol conversion was confirmed for CuOₓ/Ce₀.₆₅Zr₀.₃₅O₂ after the reaction at 150°C under 5 MPa for 3 h. The high activity of CuOₓ/Ce₀.₆₅Zr₀.₃₅O₂ was attributed to the leached copper ions, which caused a homogeneous oxidation reaction. In the case of MnOₓ/Ce₀.₆₅Zr₀.₃₅O₂, while the high conversion of phenol (94%) was obtained, phenol was mainly converted to carbonaceous deposits on the surface of the catalyst, which caused the deactivation. The high activity for the CuO-supported CeO₂-ZrO₂ was also reported by Parvas et al. (2014b), while Ni/CeO₂-ZrO₂ showed low activity (Parvas et al., 2014a).

**CATALYTIC LIQUID-PHASE OXIDATION OF PHENOL DERIVATIVES**

Up to date, effective oxidation of phenol derivatives has also been demonstrated by using CeO₂-ZrO₂-based catalysts, and their activities are summarized in Table 2. Li et al. (2007) studied the oxidation of o-chlorophenol over Ru/CeO₂-ZrO₂ solid solutions. The Ru/CeO₂-ZrO₂ catalysts have higher catalytic activities than Ru/CeO₂ and Ru/ZrO₂, because the oxygen supply to the active site from liquid phase was expected to be accelerated, where CeO₂ supported catalyst might also be affected by the formation of carbonates at the catalyst surface. Among the Ru/CeO₂-ZrO₂ systems, Ru/Ce₀.₃Zr₀.₇O₂O₂ showed the highest activity, and the complete o-chlorophenol conversion was realized (140°C, total pressure 3 MPa, 6 h). They also reported that the introduction of a small amount of Pt or Nd into the CeO₂-ZrO₂ lattice enhanced the catalytic activity, because of the formation of oxygen vacancies, which increased the reducibility and facilitated the oxygen mobility. In particular, Ru/Ce₀.₃Zr₀.₇Pt₀.₀₄O₂ showed the high total organic carbon removal of 95% compared to the Ru/Ce₀.₁₆Zr₀.₈₄O₂ case (91%) (140°C, total pressure 3 MPa, 6 h), while both catalysts could completely convert o-chlorophenol. In the absence of Ru, Ce₀.₆₂Zr₀.₃₈O₂ exhibited the high o-chlorophenol conversion of 99% under the severe conditions (140°C, total pressure 5 MPa, 24 h).

For the catalytic oxidation of bisphenol-A, most of catalysts were used in combination with strong oxidizing reagent (H₂O₂ etc.) or UV irradiation (Ohko et al., 2001; Mayani et al., 2014; Liu et al., 2016; Zhou et al., 2016). Heponiemi et al. (2015) reported the catalytic decomposition of bisphenol-A using Ag supported on CeO₂-based catalysts. The bisphenol A- abatement of Ag/CeO₂ was 51% after the reaction at 160°C for 3 h under a pressure of 2 MPa, where ca. 12% of bisphenol-A was adsorbed on the catalyst. By adding a small amount of ZrO₂ to CeO₂, the bisphenol-A removal percentage was enhanced; i.e., the removal percentage of Ag/Ce₀.₆ₕZr₀.₁₅O₂ was 76% with 1% adsorption of bisphenol-A at the same condition. Choi et al. (2017) demonstrated that the CeO₂-ZrO₂-Bi₂O₃ supported on SBA-16 catalyst exhibited the catalytic activity for bisphenol-A oxidation, and 86% of bisphenol-A conversion was achieved for Ce₀.₆₇Zr₀.₁₈Bi₀.₁₅O₂/SBA-16 even with the moderate reaction conditions of 80°C for 3 h under atmospheric pressure. Here, this conversion of Ce₀.₆₇Zr₀.₁₈Bi₀.₁₅O₂/SBA-16 was higher than that of Ce₀.₈₅Zr₀.₁₅O₂/SBA-16 (60%). This enhancement was
explained by the high oxygen release and storage abilities of CeO₂-ZrO₂, because the introduction of Bi₄O₅ into the CeO₂-ZrO₂ lattice facilitated the oxygen supply via oxygen vacancies, formed by the replacement of Ce⁴⁺ and Zr⁴⁺ sites by the lower-valent Bi³⁺ ion (Imanaka et al., 2007). Choi et al. (2017) also reported that the Ce₀.₆₇Zr₀.₃₃Bi₀.₁₃O₂/SBA-16 catalyst maintained a high conversion after three consecutive reactions without the deactivation.

CONCLUSION AND PERSPECTIVES

In this mini-review, recent studies on catalytic liquid-phase oxidation of phenolic compounds using CeO₂-ZrO₂ based catalysts are summarized. By using CeO₂-ZrO₂ as a promoter, the catalytic activity was facilitated compared to the bare oxides, such as Al₂O₃ and CeO₂. Pt/CeO₂-ZrO₂ and Ru/CeO₂-ZrO₂ catalysts exhibited high activities for phenol conversion, and the complete phenol decomposition was realized for the Ru/ZrO₂-CeO₂ (Ce/Zr = 9) catalyst under conditions of 140°C and 4 MPa. Even at the moderate conditions of 80°C and atmospheric pressure, the high phenol conversion of 91% was demonstrated by dispersing Pt and CeO₂-ZrO₂-SnO₂ into SBA-16. Noble metal free catalysts have been also developed, and phenol was completely removed using the CuO₂-CeO₂-ZrO₂ catalyst, in which the leached Cu²⁺ ions promoted the phenol oxidation by work as a homogeneous catalyst.

CeO₂-ZrO₂ was also effective for the removal of phenol derivatives. Ru/Ce₀.₆₇Zr₀.₃₃Bi₀.₁₃O₂ completely converted o-chlorophenol, and the total organic carbon removal of 95% was realized. For the bisphenol-A removal, the conversions of Ag/CeO₂-ZrO₂ and CeO₂-ZrO₂-Bi₂O₅/SBA-16 were 76% (reaction conditions: 160°C, 2 MPa, 3 h) and 86% (reaction conditions: 80°C, atmospheric pressure, 3 h), respectively.
For further perspective, it is necessary to realize complete oxidation of phenolic compounds in facile operating conditions at room temperature and under atmospheric pressure, from the viewpoint of economically, safety, and sustainably. In addition, the suppression of the deactivation, caused by the carbonaceous deposit and the metal leaching, should be considered. Since one effective method to remove the carbonaceous deposit is the complete oxidation of phenols to carbon dioxide and water, the improvement in the oxygen release ability of the promoter would be a key factor, which also leads to the high catalytic activity. For enhancing the ability of the promoter, the formation of the oxygen vacancies in the lattice might lead to the increase in reducibility and the oxygen mobility. Here, to avoid the metal leaching, the composition of the promoter should be carefully selected. Further investigations would lead to the development of novel catalysts with high efficiency for practical applications.

**AUTHOR CONTRIBUTIONS**

NN collected and read papers and wrote the manuscript. AS and P-GC collected papers and contributed to the manuscript writing. NI contributed to the paper design and also wrote the manuscript. All authors read and approved the manuscript.

**REFERENCES**

Barbier, J. Jr., Oliviero, L., Renard, B., and Duprez, D. (2005). Role of ceria-supported noble metal catalysts (Ru, Pd, Pt) in wet air oxidation of nitrogen and oxygen containing compounds. Top. Catal. 33, 77–86. doi: 10.1007/s11244-005-2509-4

Chen, H., Sayari, A., Adnot, A., and Larachi, F. (2001). Composition-activity effects of Mn-Ce-O composites on phenol catalytic wet oxidation. Appl. Catal. B Environ. 32, 195–204. doi: 10.1016/S0926-3373(01)00136-9

Choi, P. G., Kamijo, A., Nunotani, N., Nakano, T., and Imanaka, N. (2017). The effect of reaction conditions on the apparent deactivation of Mn-Ce-O composites on phenol catalytic wet oxidation. Catal. Today 307–314. doi: 10.1016/j.catct.2016.07.054

Karri, R. R., Jayakumar, N. S., and Sahu, J. N. (2017). Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon. J. Mol. Liq. 231, 249–262. doi: 10.1016/j.molliq.2017.02.003

Katzier, J. R., Pickle, H. H., and Sadana, A. (1976). An evaluation of aqueous phase catalytic oxidation. J. Water Pollut. Control Fed. 48, 920–933

Keav, S., Monteros, A. E., Barbier, J. J., and Duprez, D. (2014). Wet air oxidation of phenol over Pt and Ru catalysts supported on cerium-based oxides: resistance to fouling and kinetic modelling. Appl. Catal. B Environ. 150–151, 402–410. doi: 10.1016/j.apcata.2013.12.028

Kim, K. H., Kim, J. R., and Ihm, S. K. (2009). Wet oxidation of phenol over transition metal oxidized catalysts supported on supported hydrothermal synthesis in supercritical water. J. Hazard. Mater. 167, 1158–1162. doi: 10.1016/j.jhazmat.2009.01.110

Kulkarni, U. S., and Dixit, S. G. (1991). Destruction of phenol from wastewater by oxidation with sulfite-oxygen. Ind. Eng. Chem. Res. 30, 1916–1920. doi: 10.1021/ie00056a037

Lee, D. K., Kim, D. S., Kim, T. H., Lee, Y. K., Jeong, S. E., Le, N. T., et al. (2010). Deactivation of Pt catalysts during wet oxidation of phenol. Catal. Today 154, 244–249. doi: 10.1016/j.cattod.2010.03.052

Li, L., Chen, P., and Gloynea, E. F. (1991). Generalized kinetic model for wet oxidation of organic compounds. AIChE J. 37, 1687–1697. doi: 10.1002/ai.690371112

Li, N., Descorne, C., and Besson, M. (2007). Catalytic wet air oxidation of 2-chlorophenol over Ru loaded CeO2-ZrO2 solid solutions. Appl. Catal. B Environ. 76, 92–100. doi: 10.1016/j.apcatb.2007.05.013

Lin, S. H., Ho, S. J., and Wu, C. L. (1996). Kinetic and performance characteristics of wet air oxidation of high-concentration wastewater. Ind. Eng. Chem. Res. 35, 307–314. doi: 10.1021/ie950251u

Liu, Y., Zhu, G., Gao, J., Hojamberdev, M., Lu, H., Zhu, R., et al. (2016). A novel CeO2-Bi2Ti3O12 composite heterojunction structure with an enhanced photocatalytic activity for bisphenol A. J. Alloy. Compd. 688, 487–496. doi: 10.1016/j.jallcom.2016.07.054

Ma, C., Wen, Y., Yue, Q., Li, A., Fu, J., Zhang, et al. (2017). Oxygen-vacancy-promoted catalytic wet air oxidation of phenol from MnO2-CeO2. RSC Adv. 7, 27079–27088. doi: 10.1039/C7RA0437G

Maseide, Z. P. G., Kuster, B. F. M., Ptasiński, K. J., Janssen, F. J. J. G., Katima, J. H. Y., and Schouten, J. C. (2005). Support and dispersion effects on activity of platinum catalysts during wet oxidation of organic wastes. Top. Catal. 33, 87–99. doi: 10.1007/s11244-005-2514-4

Mayani, S. V., Zeyani, V., and Kim, S. W. (2014). SBA-15 supported Fe, Ni, Fe-Ni bimetallic catalysts for wet oxidation of bisphenol-A. Bull. Korean Chem. Soc. 35, 3533–3541. doi: 10.5021/bkcs.2014.35.12.3535

Mishra, V. S., Mahajan, V. V., and Joshi, J. B. (1995). Wet air oxidation. Ind. Eng. Chem. Res. 34, 2–48. doi: 10.1021/ie940040a001

Montini, T., Melchionna, M., Monai, M., and Fransiero, P. F. (2016). Fundamentals and catalytic applications of CeO2-based materials. Chem. Rev. 116, 5987–6041. doi: 10.1021/acs.chemrev.5b00603

Nidheesh, P. V. (2015). Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. RSC Adv. 5, 40552–40577. doi: 10.1039/C5RA02023A

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Nousir, S., Keav, S., Barbier, J. Jr., Bensitel, M., Brahmi, R., et al. (2008). Deactivation phenomena during catalytic wet air oxidation (CWAO) of phenol over platinum catalysts supported on ceria and ceria-zirconia mixed oxides. Appl. Catal. B Environ. 84, 723–731. doi: 10.1016/j.apcatb.2008.06.010

Ohko, Y., Ando, I., Niwa, C., Tatsuma, T., Yamamura, T., Nakashima, T., et al. (2001). Degradation of bisphenol A in water by TiO2 photocatalyst. Environ. Sci. Technol. 35, 2365–2368. doi: 10.1021/es0017571

Parvas, M., Haghighi, M., and Allahyari, S. (2014a). Catalytic wet air oxidation of phenol via ultrasound-assisted synthesized Ni/CeO2-ZrO2 nanocatalyst used in wastewater treatment. Arab. J. Chem. doi: 10.1016/j.arabjc.2014.10.043. [Epub ahead of print].

Parvas, M., Haghighi, M., and Allahyari, S. (2014b). Degradation of phenol aqueous solutions. A kinetic investigation. Ind. Eng. Chem. Res. 33, 3070–3077. doi: 10.1021/ie00036a023

Pintar, A., and Levec, J. (1994). Catalytic liquid-phase oxidation of phenol in facile condition using Pt/CeO2-ZrO2-SnO2 catalyst supported on mesoporous silica SBA-16. J. Environ. Chem. Eng. 5, 3999–4003. doi: 10.1016/j.jece.2017.07.072

Torres, R. A., Sarantakos, G., Combet, E., Pétrier, C., and Pulgarin, C. (2008). Sequential helio-photo-Fenton and sonication processes for the treatment of bisphenol A. J. Photochem. Photobiol. A Chem. 199, 197–203. doi: 10.1016/j.jphotochem.2008.05.016

Trovarelli, A. (1996). Catalytic properties of ceria and CeO2-containing materials. Catal. Rev. Sci. Eng. 38, 439–520. doi: 10.1080/01614949608006464

Varez, A., Garcia-Gonzalez, E., and Sanz, J. (2006). Cation miscibility in CeO2-ZrO2 oxides with fluorite structure. A combined TEM, SAED and XRD Rietveld analysis. J. Mater. Chem. 16, 4249–4256. doi: 10.1039/B607778A

Villegas, L. G. C., Mashhadi, N., Chem, M., Mukherjee, D., Taylor, K. E., and Biswas, N. (2016). A short review of techniques for phenol removal from wastewater. Curr. Pollution Rep. 2, 157–167. doi: 10.1007/s40726-016-0035-3

Wang, L., Zhu, W., Yang, S., Wang, W., and Zhou, Y. (2008). Catalytic wet air oxidation of phenol with pelletized ruthenium catalysts. Appl. Catal. B Environ. 78, 30–37. doi: 10.1016/j.apcatb.2007.08.014

Yashima, M., Arashi, H., Kakihana, M., and Yoshimura, M. (1994). Raman scattering study of cubic-tetragonal phase transition in \( \text{Zr}_{1-x}\text{Ce}_x\text{O}_2 \) solid solution. J. Am. Ceram. Soc. 77, 1067–1071. doi: 10.1111/j.1151-2916.1994.tb07270.x

Yasuda, K., Yoshimura, A., Katsuma, A., Masui, T., and Imanaka, N. (2012). Low-temperature complete combustion of volatile organic compounds over novel \( \text{Pt/CoO}_2\text{Zr}_2\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3 \) catalysts. Bull. Chem. Soc. Jpn. 85, 522–526. doi: 10.1246/bcsj.20110382

Zhang, N., Xian, G., Li, X., Zhang, P., Zhang, G., and Zhu, J. (2018). Iron based catalysts used in water treatment assisted by ultrasound: a mini review. Front. Chem. 6:12. doi: 10.3389/fchem.2018.00012

Zhou, Q., Xing, A., Li, J., Zhao, D., Zhao, K., and Lei, N. (2016). Synergistic enhancement in photoelectrocatalytic degradation of bisphenol A by CeO2 and reduces graphene oxide co-modified TiO2 nanotube arrays in combination with Fenton oxidation. Electrochim. Acta 209, 379–388. doi: 10.1016/j.electacta.2016.05.094

Zimmermann, F. J. (1958). New waste disposal process. Chem. Eng. 25, 117–120.

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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