Nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ Catalytic Powders for *m*-Xylene and Toluene Combustion

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The bee's nest-like nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ powders were synthesized by combustion method using polyvinyl alcohol as a fuel and their catalytic activity were tested in the *m*-xylene and toluene combustion. The results showed that the catalytic reaction temperature increased monotonically from 200 to 250°C and from 250 to 300°C for the 90% conversion of *m*-xylene and toluene, respectively, with the calcination temperature in the range of 450–850°C. For both combustions, the sample calcined at 450°C with a bee's nest-like nanostructure and average pore size of 800 nm exhibited the highest catalytic activity. Among the samples calcined at 850°C, the lowest catalytic reaction temperature for the 90% conversion of *m*-xylene and toluene of 250 and 300°C, respectively, was found with the sample having the equimolar ratio of Ce/Al. [\[doi:10.2320/matertrans.M2013056\]](https://doi.org/10.2320/matertrans.M2013056)

(Received February 12, 2013; Accepted April 3, 2013; Published May 25, 2013)

Keywords: nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$, catalyst, *m*-xylene combustion, toluene combustion, combustion method

1. Introduction

In the field of organic pollutant treatment, the elimination of volatile organic compounds (VOCs), especially carcinogens like benzene, ethylbenzene, xylene and toluene, has been studied intensively.^{1–3)} For the combustion of these compounds, the catalytic combustion was frequently used due to the fact that it exhibits high conversion efficiency and causes no side toxic pollutants. To eliminate *m*-xylene and toluene, in particularly, one of the current research trends is finding low cost alternatives, for examples, carbon-based materials, mixed oxides, ... to commonly used noble metal-based catalysts.^{4–6)} Among these materials, ceria and ceria-based mixed oxides such as $\text{MnO}_x\text{--CeO}_2/\text{TiO}_2$, CuO/CeO_2 , $\text{CuO--CeO}_2/\text{Al}_2\text{O}_3$... were already investigated.^{7–11)} Owing to the high oxygen storage capacity of CeO_2 and the high surface area and thermal stability of Al_2O_3 , $\text{CeO}_2\text{--Al}_2\text{O}_3$ mixed oxide system were used as catalysts for the oxidation of toxic gases such as NO and CO.^{12,13)} Recently, nanostructured Pt/ $\text{CeO}_2\text{--Al}_2\text{O}_3$ catalysts were reported to be used for total oxidation of VOCs including toluene and mixed xylene.¹⁴⁾ To date, to our knowledge, no work has been reported on using for the $\text{CeO}_2\text{--Al}_2\text{O}_3$ system as a catalyst for *m*-xylene while for the case of toluene only one research has been published.¹⁵⁾

In this work the catalytic activity in the *m*-xylene and toluene combustion of the bee's nest-like nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ powders synthesized by combustion method using polyvinyl alcohol and metal nitrates as starting materials was presented. The effects of calcination temperature and Ce/Al ratio on the *m*-xylene and toluene conversion of samples were also investigated.

2. Experimental

2.1 Synthesis of catalyst

The synthesis of nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ powders by combustion methods from metal nitrates and polyvinyl

alcohol was described elsewhere.¹⁶⁾ In a typical procedure, analytical grade nitrates of cerium and aluminium ions with desired Ce/Al molar ratio were dissolved in a solution of PVA with the metal cations/PVA molar ratio fixed at 1/3. The mixture was adjusted to the pH of 4 and then heated at 80°C until a viscous gel was obtained. This gel was calcined at 450, 600, 750 and 850°C for 2 h. The morphology of prepared samples was characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S 4800 microscope).

2.2 Catalytic activity test

The prepared samples with different calcination temperatures and Ce/Al molar ratios were tested for *m*-xylene and toluene combustion. For combustion experiments, a 0.2 g of samples was loaded inside a micro-flow reactor with the catalytic layer thickness of 0.6 cm. Then, 2000 ppm of saturated *m*-xylene or toluene vapour in dry air was passed through catalytic layer with the flowing rate of 10 ml/min. The catalytic reactions of *m*-xylene and toluene were carried out at temperatures in the range from 50 to 400°C. The conversion rate of these two compounds can be calculated from following formula:

$$R_{\text{VOC}} = [(C_{\text{VOC(in)}} - C_{\text{VOC(out)}})/C_{\text{VOC(in)}}] \times 100\%$$

where, R_{VOC} (%) is the conversion rate of *m*-xylene or toluene; $C_{\text{VOC(in)}}$ and $C_{\text{VOC(out)}}$ are the *m*-xylene or toluene concentrations in the inlet and outlet gas, respectively.

3. Results and Discussion

3.1 Synthesis of the bee's nest-like nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ powders

The structural, morphological properties and the effects of preparative conditions including the Ce/Al molar ratio and calcination temperature on phase formation, phase composition and morphology of the bee's nest-like nanostructured $\text{CeO}_2\text{--Al}_2\text{O}_3$ powders were described in details in Ref. 16). It was found that for samples with Ce/Al molar ratio of 5/5 calcined at temperatures below 750°C, no crystalline phases were detected and the pure fluorite structure $\text{CeO}_2\text{--}$

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Fig. 1 FE-SEM images at the magnification of (a) 10000 and (b) 80000 of $\text{CeO}_2\text{-Al}_2\text{O}_3$ sample with Ce/Al molar ratio of 5/5 calcined at 450°C.

based phase fully crystallized was obtained only when the calcination temperatures of over 850°C. In addition, the bee's nest-like nanostructure was observed in samples calcined at temperatures in the range of 500–850°C and no longer existed for the samples calcined at 950°C. In the present work, the bee's nest-like nanostructure with three-dimensional pore arrangement was also found in the sample with Ce/Al molar ratio of 5/5 calcined at 450°C (Fig. 1(a)), the temperature from which no further changes in thermogravimetric (TG) curve was found.¹⁶⁾ The average pore size of this sample is 800 nm (Fig. 1(b)) and larger than those of samples calcined at higher temperatures.

3.2 Effects of calcination temperature on the *m*-xylene and toluene conversion

The prepared samples with Ce/Al molar ratio of 5/5 calcined at 450, 600, 750 and 850°C were tested for catalytic activity in *m*-xylene and toluene conversion. From Fig. 2(a) one can realize that, for the case of *m*-xylene combustion, with the same conversion efficiency of 90%, the catalytic reaction temperature increased monotonically from 200 to 250°C with the calcination temperature ranging from 450 to 850°C. Similarly, for the toluene combustion, the conversion efficiency of 90% was obtained at temperatures in the range of 250–300°C for the sample calcined at 450–850°C, respectively (Fig. 2(b)). Compared to non-noble metal

Fig. 2 Catalytic conversion of (a) *m*-xylene and (b) toluene over nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders with Ce/Al molar ratio of 5/5 calcined at 450, 600, 750 and 850°C.

catalyst systems such as activated carbon fibre impregnated with transition metals (Co, Cr, Ni and Cu) for the *m*-xylene catalytic combustion, the catalytic reaction temperature of the present catalytic system was lower for the sample calcined at 450°C and was nearly the same for the sample calcined at 850°C.⁵⁾ The catalytic reaction temperature of 200°C required for 90% conversion of nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders calcined at 450°C for *m*-xylene catalytic combustion was also lower than that of active CeO_2 catalyst for *p*-xylene (230°C) oxidation and of CeO_2 nanocubes for *o*-xylene conversion (210°C) and was equal to that of nanostructured Pt/ $\text{CeO}_2\text{-Al}_2\text{O}_3$ catalysts for mixed xylene combustion.^{7,8,15)} Thus, it is reasonable to use our nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders with high content of Al (Ce/Al molar ratio of 5/5) for *m*-xylene combustion due to their high catalytic activity and cost effectiveness. For the toluene combustion, the required temperature for 90% conversion of the bee's nest-like nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders was lower for the sample calcined at 450°C and, for the sample calcined at 850°C, was closed to that reported for Pt/ $\text{CeO}_2\text{-Al}_2\text{O}_3$ nanocatalysts and for the $\gamma\text{-Al}_2\text{O}_3\text{-CeO}_2$ mixed oxide system prepared by the impregnation of boehmite with cerium nitrate and followed by calcinations.^{14,15)} However, the toluene conversion efficiency of the studied samples was still slightly lower than that observed for active CeO_2 catalyst.⁸⁾ From above studies, the highest catalytic activity in both *m*-xylene and toluene combustions obtained for the sample calcined at 450°C in comparison to that of other bee's nest-like nanostructured samples calcined at 600, 750 and 850°C might be attributed to its largest average pore size of 800 nm.

Fig. 3 Catalytic conversion of (a) *m*-xylene and (b) toluene over nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders calcined at 850°C with Ce/Al molar ratio of 1/9, 2/8, 3/7, 4/6 and 5/5.

3.3 Effects of Ce/Al molar ratio on the *m*-xylene and toluene conversion

In order to investigate the effects of Ce/Al molar ratio on the *m*-xylene and toluene conversion, we intend to select $\text{CeO}_2\text{-Al}_2\text{O}_3$ mixed oxide powders that exhibit a stable bee's nest-like nanostructure and well-defined fluorite structure CeO_2 -based phase. From the results reported in our previous work,¹⁶⁾ it was clear that the sample calcined at 850°C is the only one that possesses both the bee's nest-like nanostructure and the pure fully crystallized fluorite structure CeO_2 -based phase. Hence, the samples calcined at 850°C with the Ce/Al molar ratio of 1/9, 2/8, 3/7, 5/5 and 4/6 were subjected to catalytic activity tests for *m*-xylene and toluene combustion (Figs. 3(a) and 3(b)). The results showed that, the lowest required temperatures for 90% conversion of *m*-xylene and toluene were 250 and 300°C , respectively, and was found in the sample with Ce/Al molar ratio of 5/5. Thus, for the case of toluene conversion, the optimized Ce/Al molar ratio was found for the lowest catalytic reaction temperature and this differs from the previous work,¹⁵⁾ in which the lowest value

of catalytic reaction temperature was achieved with the highest Ce/Al ratio.

4. Conclusion

In conclusion, the bee's nest-like nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders were successfully synthesized by combustion method using polyvinyl alcohol as a fuel was studied. Results showed that, for the samples calcined at temperatures in the range of $450\text{--}850^\circ\text{C}$, the catalytic reaction temperature increased monotonically from 200 to 250°C and from 250 to 300°C for the 90% conversion of *m*-xylene and toluene, respectively. For these combustions, the sample calcined at 450°C with a bee's nest-like nanostructure and average pore size of 800 nm exhibited the highest catalytic activity. Among the samples with different investigated Ce/Al molar ratios of 1/9, 2/8, 3/7, 4/6 and 5/5, the lowest catalytic reaction temperature for the 90% conversion of *m*-xylene and toluene of 250 and 300°C , respectively, was found with the sample having the equimolar ratio of Ce/Al. From these promising results, it is quite possible to use the bee's nest-like nanostructured $\text{CeO}_2\text{-Al}_2\text{O}_3$ powders as catalyst for elimination of *m*-xylene and toluene as well as other volatile organic compounds.

REFERENCES

- 1) J. C. S. Wu, Z. A. Lin, F. M. Tsai and J. W. Pan: *Catal. Today* **63** (2000) 419–426.
- 2) S. Al-Khattaf, M. N. Akhtar, T. Odedairo, A. Aitani, N. M. Tukur, M. Kubů, Z. Musilová-Pavlačková and J. Čejka: *Appl. Catal. A* **394** (2011) 176–190.
- 3) W. Xie, Y. Qin, D. Liang, D. Song and D. He: *Ultrason. Sonochem.* **18** (2011) 1077–1081.
- 4) A. F. Pérez-Cadenas, S. Morales-Torres, F. J. Maldonado-Hódar and F. Carrasco-Marín: *Appl. Catal. A* **366** (2009) 282–287.
- 5) V. Gaur, A. Sharma and N. Verma: *Carbon* **43** (2005) 3041–3053.
- 6) I.-J. Lee, C.-H. Lee, S.-D. Lee and D. J. Suh: *J. Ind. Eng. Chem.* **11** (2005) 918–925.
- 7) L. He, Y. Yu, C. Zhang and H. He: *J. Environ. Sci.* **23** (2011) 160–165.
- 8) C.-H. Wang and S.-S. Lin: *Catal. A* **268** (2004) 227–233.
- 9) D. Yu, Y. Liu and Z. Wu: *Catal. Commun.* **11** (2010) 788–791.
- 10) R. Prasad and G. Rattan: *Bull. Chem. React. Eng. Catal.* **5** (2010) 7–30.
- 11) U. Menon, V. V. Galvita and G. B. Marin: *J. Catal.* **283** (2011) 1–9.
- 12) Y. Chen, S. Zhu, T. Qiu and S. Chen: *Catal. Commun.* **11** (2009) 20–23.
- 13) P. A. Deshpande, S. T. Aruna and G. Madras: *Catal. Sci. Technol.* **1** (2011) 1683–1691.
- 14) Z. Abbasi, M. Haghighi, E. Fatehifar and S. Saedy: *J. Hazard. Mater.* **186** (2011) 1445–1454.
- 15) G. Del Angel, J. M. Padilla, I. Cuauhtémoc and J. Navarrete: *J. Mol. Catal. A: Chem.* **281** (2008) 173–178.
- 16) D. N. Nhiem, L. M. Dai, Ng-D. Van and D. T. Lim: *Ceram. Int.* **39** (2013) 3381–3385.