The enhancement effect of acid treatment on the Mn_2O_3 catalyst for toluene oxidation

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Abstract: The effect of acid treatment on manganese oxides samples has been investigated for the catalytic oxidation of toluene. It was found that the acid leaching not only enhanced the toluene conversion and specific reaction rate of catalysts largely, but also lowered the activation energy distinctly. According to results of Raman, SEM, XPS, O_2-TPD and H_2-TPR, the acid leaching can induce the formation of abundant defects and active oxygen species, further improving the mobility of surficial oxygen species and the low-temperature reducibility of catalysts, which is indispensable for the enhanced toluene oxidation.

Keywords: acid treatment, enhancement effect, toluene oxidation

1. Introduction

Most volatile organic compounds (VOCs), such as formaldehyde, benzene and toluene, can cause serious harm to both the human health and environment.[1, 2] Catalytic oxidation is considered as a promising technique for VOCs abatement among the various treatment methods, because of its energy saving, high efficiency and environmental friendliness.[3] The transition metal oxides with low cost, high thermal stability and chemical composition diversity have attracted great attentions recently and become the very promising and versatile catalysts in VOCs oxidation reactions.[4] However, it is still a challenging subject to improve the air purification ability of transition metal oxides.

Recent studies have proved that the acid treatment is an effective means to change the surficial chemical properties of catalysts such as metal oxidation state, active oxygen species or exposure defects, which is indispensable for high-efficiency catalysts.[5, 6] Quiroz et al. reported that the acid treatment could alter the oxidation state of manganese and greatly improve the conversion of formaldehyde and the intrinsic reaction.[5] Lee et al. leached $Na_{0.44}MnO_2$ nanowires in acid and successfully introduced the controllable defect in catalysts.[6] Herein, we prepared a series of acid treated manganese oxides (Mn_2O_3) with different concentrations and investigated the effect of acid treatment on toluene catalytic behavior.

2. Experimental

The precursor of manganese oxide was prepared by hydrothermal method as reported by Joel Henzie et al.[7] In detail, 1.648 g PVP was dissolved in a 35 mL DMF, and then 50 wt % aqueous $Mn(NO_3)_2$ solution was added under the magnetic stirring to form a homogeneous solution. After that, the solution was kept in a 100 mL autoclave with a Teflon liner at 180 ºC for 6 h. When cooling to room temperature, the black precipitate was washed with DMF, dried in a vacuum oven at 60 ºC, and finally calcined at 500 ºC for 4 h, denoted as A-0. The calcined samples were treated with an aqueous solution of H_2SO_4 (2.5, 5, 10, 15 mol/L) by stirring in a beaker for 1 h. The final product was centrifuged, washed and dried at 105 ºC. The obtained samples were denoted as A-x, in which the x represents the concentration of H_2SO_4.

3. Results and discussion

Table 1 Physical-chemical and toluene catalytic properties of A-x catalysts

samples	S_{BET} (m^2/g)	V_p (cm^3/g)	O_{ads}/O_{latt}	Mn^{3+}/Mn^{4+}	Rs (mmol h^{-1} m^{-2})	Ea (kJ/mol)
A-0	6.4	0.033	0.43	3.33	3.33×10^{-3}	253.7
A-2.5	8.7	0.049	0.88	1.47	8.17×10^{-3}	223.5
A-5	9.9	0.051	1.30	1.30	8.96×10^{-3}	161.8

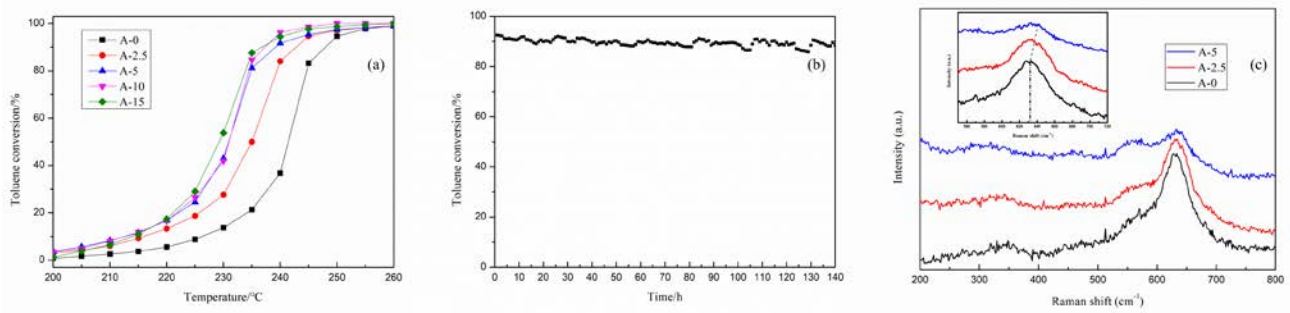

Figure 1. (a) Toluene conversion of A-x catalysts, (b) the stability test of A-5 at 245 ºC and (c) Raman spectra of A-x catalysts.

As presented Figure 1a, the acid leaching could improve the catalytic performance of catalysts largely, especially for the sample acid-treated with low concentration. The low acid concentration (< 5 mol/L) resulted in the large increase of toluene catalytic activity, while further increasing the acid-treated concentration did not promote the improvement of the toluene catalytic activity for the toluene oxidation. In order to investigate the effect of acid treatment on the catalytic performance deeply, the reaction kinetics of A-x samples were measured. Table 1 showed that the specific toluene reaction rates increased from 3.33×10^{-3} to 8.96×10^{-3} mmol h^{-1} m^{-2} and the activation energy decreased from 253.7 to 161.8 kJ/mol with the increase of acid concentration from 0 to 5 mol/L. It is generally agreed that the specific reaction rate and activation energy is related to the intrinsic catalytic activity.[8] Therefore, we speculated that acid treatment could significantly enhance intrinsic catalytic efficiency. In addition, A-5 sample exhibited an excellent stability and no significant deactivation was observed even over a 140 h long test in the same test conditions, as can be seen from Figure 1b.

XRD, BET, EM and Raman results revealed that the abundant defects in samples were induced by acid treatment, though the crystal structure, crystalline size and surface area were essentially unchanged. According to results of XPS, O_2-TPD and H_2-TPR, the acid leaching can not only induce the formation of abundant active oxygen species, but also improve the mobility of surficial oxygen species and the low-temperature reducibility of catalysts, which is indispensable for the enhanced toluene oxidation. In situ DRIFTS results indicated that the toluene was sequentially oxidized to alkoxide, benzaldehyde, benzoate, maleic anhydride species, and finally to CO_2, needing plentiful active oxygen species to participate. Importantly, the abundant defects induced by acid leaching can rapidly activate, transfer and replenish oxygen species, improving the catalytic performance of acid treated samples fundamentally.

4. Conclusions

In this work, we prepare a series of acid treated manganese oxides used different concentration and investigate the effect of acid treatment on toluene catalytic behavior. It was found that the acid leaching not only enhanced the toluene conversion and specific reaction rate of catalysts largely, but also lowered the activation energy distinctly. The various characterization results revealed that acid treatment could induce abundant defects and active oxygen species, and also improve the mobility of surficial oxygen species and the low-temperature reducibility, which is vital for the enhancement effect of catalytic performance. Our findings shed light on the enhancement effect of acid treatment on toluene catalytic oxidation, which may open a new strategy for the design of high-efficiency catalyst.

References

1. P. Sun, W. Wang, X. Dai, X. Weng and Z. Wu, *Appl. Catal., B*, 2016, **198**, 389-397.
2. A. K. Sinha, K. Suzuki, M. Takahara, H. Azuma, T. Nonaka and K. Fukumoto, *Angew. Chem., Int. Ed.*, 119 (2007), 2949.
3. H. B. Huang, Y. Xu, Q. Y. Feng and D. Y. C. Leung, *Catal. Sci. Technol.*, 5 (2015), 2649.
4. Y. Liu, H. Dai, J. Deng, Y. Du, X. Li, Z. Zhao, Y. Wang, B. Gao, H. Yang and G. Guo, *Appl. Catal., B*, 140-141 (2013), 493.
5. J. Quiroz, J. M. Giraudon, A. Gervasini, C. Dujardin, C. Lancelot, M. Trentesaux and J. F. Lamonier, *ACS Catal.*, 5 (2015), 2260.
6. J.-H. Lee, R. Black, G. Popov, E. Pomerantseva, F. Nan, G. A. Botton and L. F. Nazar, *Energy & Environmental Science*, 5 (2012), 9558.
7. J. Henzie, V. Etacheri, M. Jahan, H. Rong, C. N. Hong and V. G. Pol, *J. Mater. Chem. A*, 5 (2017), 6079.
8. X. Yang, X. Yu, M. Lin, M. Ge, Y. Zhao and F. Wang, *J. Mater. Chem. A*, 5 (2017), 13799.