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Low-temperature oxidation removal of formaldehyde catalzsed by Mn-containing mixed oxides supported BiOCl in air

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1. Introduction

Formaldehyde is one of the most harmful gases among volatile organic pollutants (VOCs), which had been listed as the first carcinogen by the international agency for research on cancer (IARC) in 2004. Among various formaldehyde removal technologies, catalytic oxidation can completely decompose formaldehyde into harmless CO_2 and H_2O without secondary pollution, and thus attracted much attention [1]. The key of this technology is to design efficient catalysts and catalytic system.

Owing to the low cost and rich resources, the transition metal catalysts are more valuable for the practical application. Among them, manganese oxides, especially the Mn-containing mixed oxides usually exhibited excellent catalytic performance in the oxidation removal of formaldehyde than the other transition metal oxides [2,3]. Kim et al. reported $MnOx/TiO_2$ catalyst could completely catalytically oxidize formaldehyde with O_3 at room temperature. Zhu et al. found that MnO_xCeO_2 composite catalyst achieved complete formaldehyde conversion at 100 ^oC in air. On the other hand, BiOCl is a kind of layered semiconductor with high anisotropy and thermal stability, which had been used wildly in photocatalytic degradation of organic pollutants [4]. Our consistent interest in the design of heterogeneous catalysts and the removal of organic pollutants pushed us to combine the catalytic characteristics of mixed manganese oxide and BiOCl. Here, we tried to load active BiOCl on the Mn-containing mixed oxides and their parent hydrotalcites. The catalytic performance and reusability of the obtained catalysts in the oxidation removal of formaldehyde were investigated, and the structure activity relationship of catalysts and catalytic path of this removal reaction were also discussed.

2. Methods

Typically, aqueous solution A containing a certain amount of $Mn(NO_3)_2•6H_2O$, $Mg(NO_3)_2•6H_2O$ and $Al(NO_3)_3•9H_2O$, solution B containing a certain amount of $BiCl_3$, and aqueous solution C containing a certain amount of Na_2CO_3 were prepared firstly. Then, the solution A and B were simultaneously added dropwise to the solution C with stirring at 80 ℃. The pH value of the mixture was maintained in 10.0±0.5 by adding appropriate amount of NaOH. The resulting gel-like slurry was further aged for 12 h at room temperature, and then was filtered, washed. The filtrate was dried in air at 373 K for 12 h, and was

designated as *x*BiOCl/MnMgAl-HT. The as-prepared solid sample was further calcined at 450 ℃ under N_2 for 8 h, which was designated as *x*BiOCl/MnMgAlO (x: the loading amount of BiOCl).

3. Results and discussion

XRD, SEM, TEM and TG characterization confirmed that the crystal structure of BiOCl was still intact after calcination, simultaneously mixed oxides formed in *x*BiOCl/MnMgAlO. The N_2 adsorption/desorption isotherms of *x*BiOCl/MnMgAl-HT and *x*BiOCl/MnMgAlO showed type IV isotherms, indicating that mesoporous structures had been formed due to the aggregation of particles. A significant increase was found in the surface area of *x*BiOCl/MnMgAlO in comparison with that of *x*BiOCl/MnMgAl-HT. It should be noted that H_2-TPR and XPS illustrated a significant different chemical state of Mn present in *x*BiOCl/MnMgAl-HT and *x*BiOCl/MnMgAlO. XPS spectra of Bi 4f of the supported BiOCl catalysts also displayed that the oxygen vacancy occurred derived from the interaction of BiClO and supports.

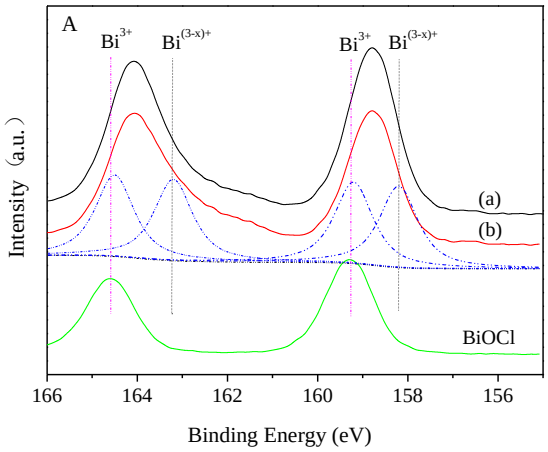

Figure 1. XPS spectra of Bi 4f

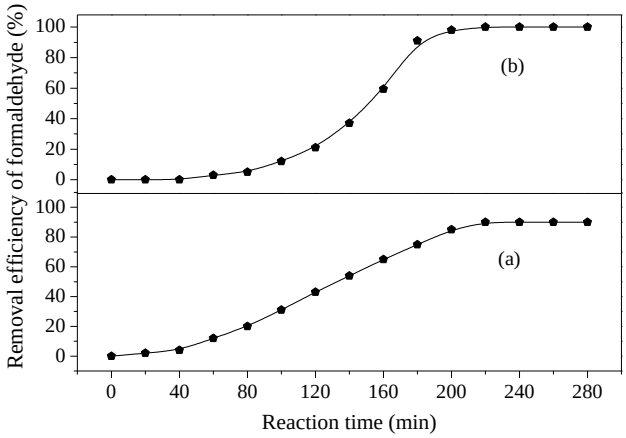

Figure 2. Catalytic performance of catalysts

(a) *0.01*BiOCl/MnMgAl-HT, (b) *0.01*BiOCl/MnMgAlO

The catalytic performance of the obtained supported catalysts was investigated in the oxidation removal of formaldehyde in detail. The results revealed that *x*BiOCl/MnMgAl-HT and *x*BiOCl/MnMgAlO were active catalysts, while the pure BiOCl, MnMgAl-HT and MnMgAlO only showed poor catalytic activity in the removal of formaldehyde. Moreover, *x*BiOCl/MnMgAlO exhibited much higher catalytic performance than *x*BiOCl/MnMgAl-HT, which was attributed to their different surface adsorption capacity to reactant formaldehyde confirmed by in-situ FTIR, and to their different redox capacity confirmed by H_2-TPR. The structure activity relationship of catalyst was also explored by infrared in-situ technology. It was found that the synergetic catalysis among the oxygen vacancies, surface properties and chemical state of Mn could afford the efficient catalytic performance of BiOCl/CuNiAlO. In addition, a possible reaction mechanism was also proposed.

4. Conclusions

The Mn-containing mixed oxides supported BiOCl was a promising catalyst in Low-temperature oxidation removal of formaldehyde in air. The complete removal efficiency of formaldehyde could be achieved at 70 ^{o}C and 200 min, and the catalysts can be reused at least ten times. Such a high catalytic performance could be attributed to the synergetic catalysis among the chemical state of Mn, oxygen vacancies, surface properties of the supported catalyst.

References

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