

CeO₂-MnO_x composite loaded on Al₂O₃ as catalyst for HCl oxidation

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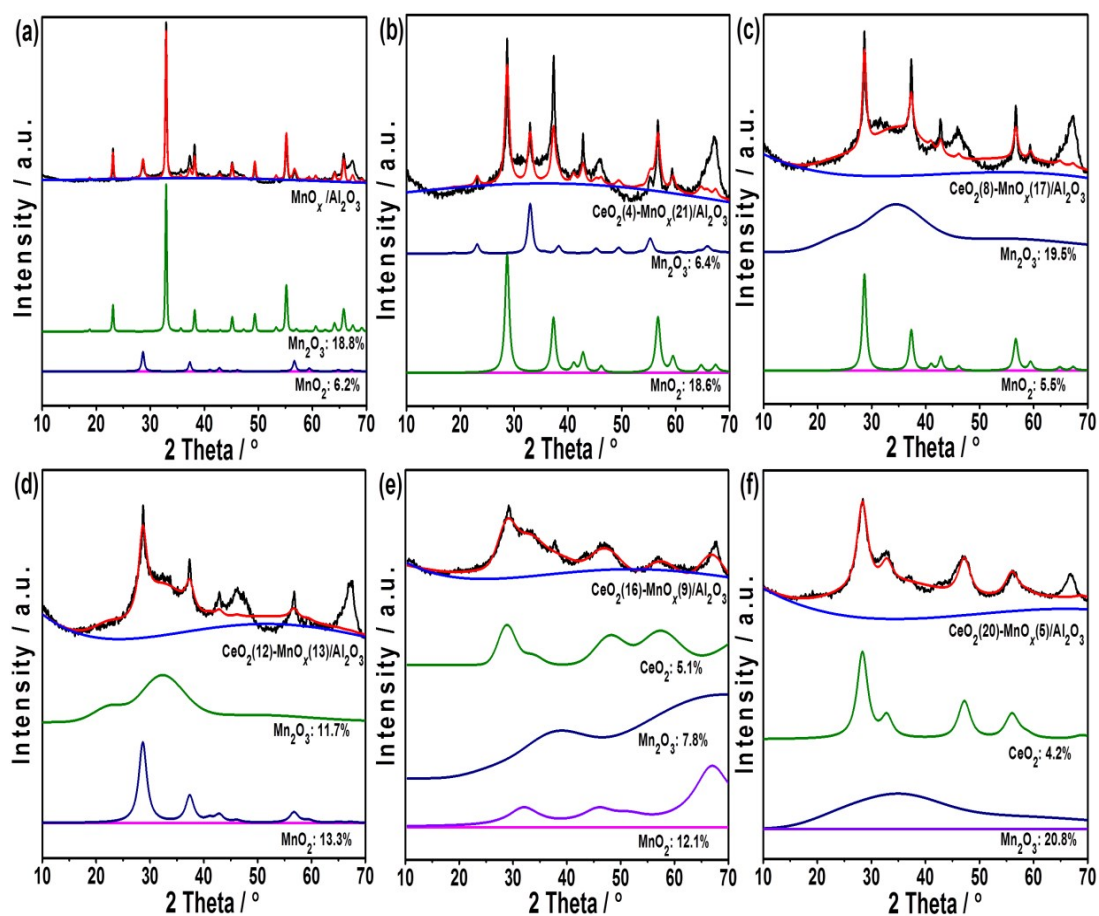


Figure S1. Rietveld analysis of XRD patterns for CeO₂-MnO_x/Al₂O₃ catalysts with various compositions.

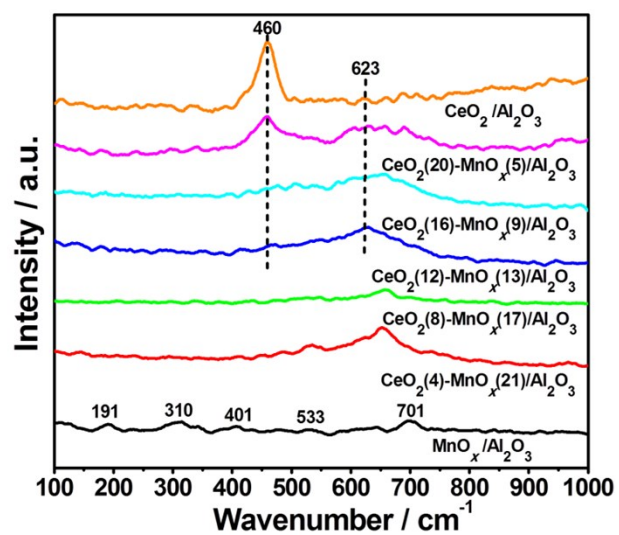


Figure S2. Raman patterns of $\text{CeO}_2\text{-MnO}_x/\text{Al}_2\text{O}_3$ catalysts with various compositions.

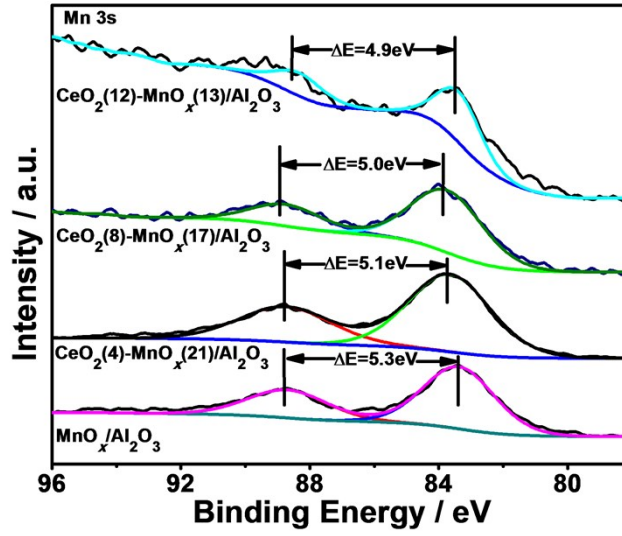


Figure S3. Mn 3s XPS spectra of $\text{CeO}_2\text{-MnO}_x/\text{Al}_2\text{O}_3$ catalysts with various compositions.

According to literature [1], the chemical state of manganese can be calculated from the binding energy gap (ΔE) between two peaks of the Mn 3s XPS spectrum. And the ΔE value related to Mn^{3+} and Mn^{4+} were evaluated to be 5.2 eV and 4.7 eV, respectively [2, 3]. In **Figure S3**, it is found that the ΔE values of the catalysts with $\text{MnO}_x:\text{CeO}_2 > 1$ are ranged in 5.1–4.9 eV, suggesting the co-existence of Mn^{4+} and Mn^{3+} . And the higher Ce doping amount leads to the more Mn^{4+} ions.

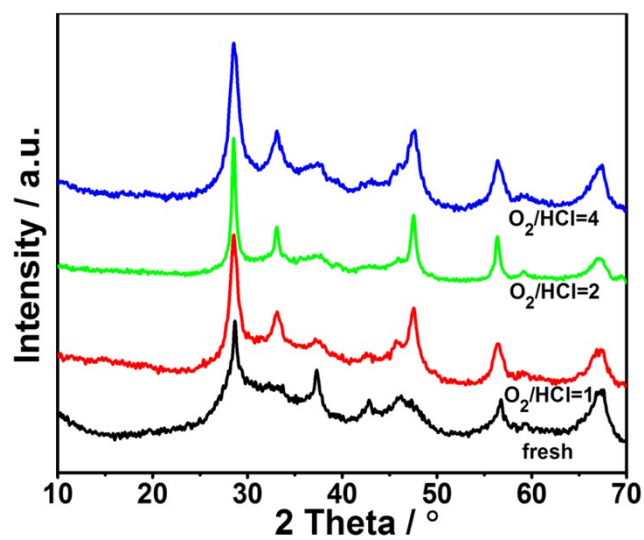


Figure S4. XRD patterns of used $CeO_2(12)-MnO_x(13)/Al_2O_3$ catalysts under different feed

O_2/HCl ratio in comparison with fresh $CeO_2(12)-MnO_x(13)/Al_2O_3$ sample. Conditions: $W_{cat} = 0.5$

g, $F_{HCl} = 16$ ml/min, $F_T = 160$ ml/min, $T = 430$ °C, $P = 1$ bar.

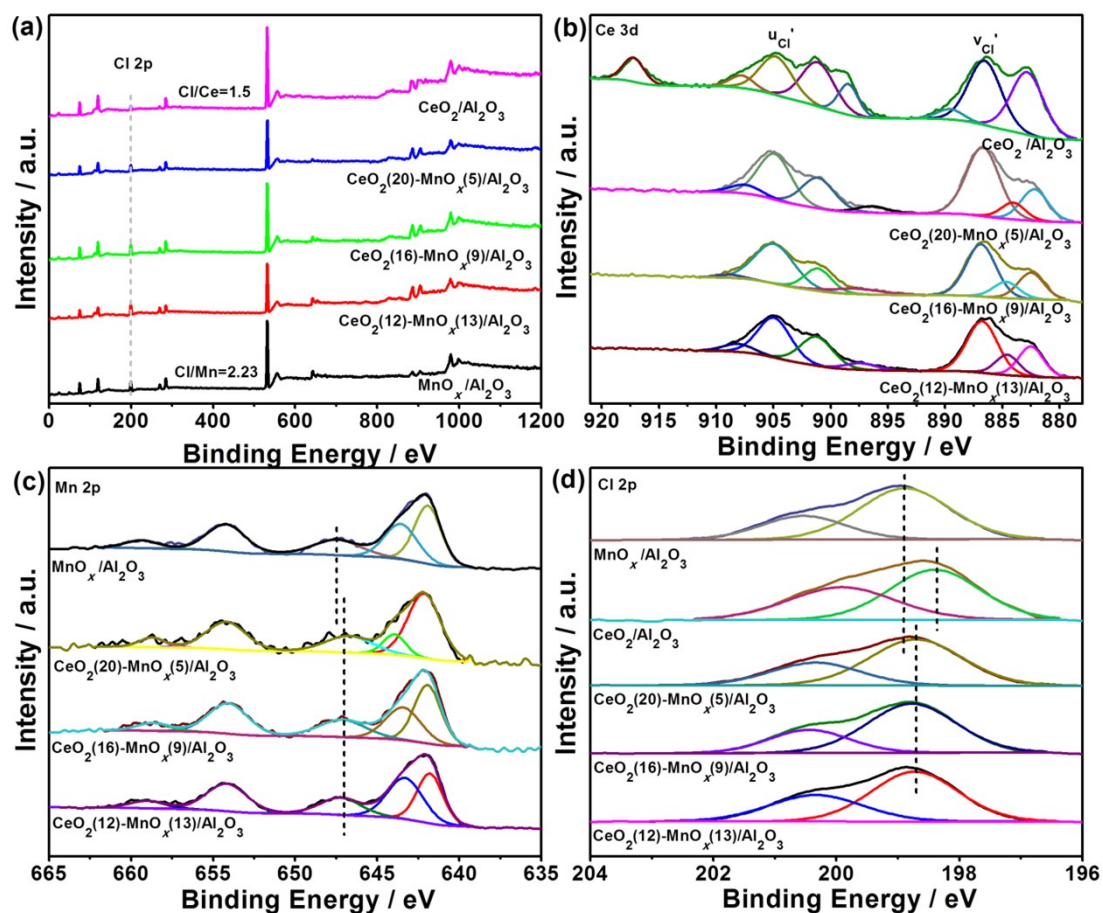


Figure S5. XPS spectra of survey (a), Ce 3d (b), Mn 2p (c) and Cl 2p (d) of $\text{CeO}_2\text{-MnO}_x/\text{Al}_2\text{O}_3$

catalysts with various compositions.

A new peak in the survey spectrum at about 198 eV confirms the presence of Cl on the surface of catalyst (**Figure S5a**) [4]. For CeO₂/Al₂O₃ catalyst exposed under pure HCl atmosphere (**Figure S5b**), the Ce³⁺ peaks at v' and u' shift to higher binding energy by about 1.8 eV, confirming the formation of CeCl₃•6H₂O [5]. For MnO_x/Al₂O₃ catalyst exposed under HCl (**Figure S5c**), the peaks of different price state manganese move to the position of higher binding energy position. For the catalysts with MnO_x percentage less than 13%, the XPS peaks of Ce 3d can not be deconvoluted regularly (**Figure S5b**). Although the peak of CeCl₃•6H₂O appears, the peaks of Ce⁴⁺ also shift, which may be caused by the introduction of Mn ions. By deconvolution of the Mn 2p XPS spectrum (**Figure S5c**), the peaks shift of the catalysts with MnO_x percentage less than 13% was attenuated compared that of used MnO_x/Al₂O₃, and there is still a large deviation compared to the fresh catalysts, especially the deviation of Mn⁴⁺ up to 2.2 eV. Through the analysis of the Cl 2p XPS spectrum, more useful information seems to be available (**Figure S5d**). The peak of Cl 2p at about 198 eV of the catalysts with high content of CeO₂ indicates that Cl bind to the catalyst surface, with a preference for manganese. The concentration of chlorine accommodated on the catalyst surface was quantified by XPS, and the ratio of Cl/Ce and Cl/Mn were 1.5 and 2.23 for used CeO₂/Al₂O₃ and used MnO_x/Al₂O₃, respectively (**Figure S5a**). This result further confirms that more chlorine tends to occupy surface sites on manganese oxides than ceria. From the XRD and XPS analysis results, it can be seen that the introduction of manganese improves the chlorine adsorption, both on the bulk and surface, and the adsorption of HCl is an important step in the HCl oxidation reaction [6].

References:

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