Electronic metal-support interaction effects and toluene combustion performance of Pt/MnO_2 catalysts with different electronic properties.

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Keywords: Electronic metal-support interaction, platinum-based catalyst, Toluene
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Abstract

Electronic metal–support interactions (EMSI) have a significant effect on the performance of Pt based catalysts for volatile organic compound (VOC) elimination. Herein, the strength of the EMSI of Pt/MnO_2 between Pt and MnO_2 support is controlled by using different Pt species, and the Pt-supported MnO_2 catalyst performed the best activity for the catalytic combustion of toluene. Through STEM-EELS, it was revealed that electrons move from Pt to MnO_2. Furthermore, it was clarified that this electron transfer promotes the mobility of lattice oxygen, and improves catalytic performance. This work provides a new idea for exploring the relationship between EMSI and efficient catalytic performance of VOC.

1. Introduction

In the study of catalytic combustion for removal of volatile organic compound (VOC), the Pt-based catalysts have been studied as the most optimal materials due to its excellent low-temperature catalytic performance. Extensive research studies have been conducted on morphological controlling, particles size tuning, and strong metal–support interaction (SMSI) to enhance their catalytic performance. Recently, electronic metal–support interaction (EMSI), a new type of MSI, has attracted an ever-increasing attention in the field of catalysis. The EMSI, associated charge transfer at the interface between the metal and the support, could tailor the electronic and chemical properties of the active sites to improve the activity of the supported catalysts[1)]. It is also expected to provide a more specific interpretation than classical SMSI in elucidating the factors responsible for the performance enhancement and the reaction mechanism. In this study, we prepared a Pt/MnO_2 catalyst for toluene combustion and attempted to improve the catalytic performance by controlling the strength of EMSI. In addition, we clarified the relationship between the EMSI and the catalytic performance.

2. Experiment

As Pt/MnO_2 catalysts with different electronic properties, we prepared supported Pt nanoparticles catalyst (Pt_{NPs}/MnO_2), supported Pt single-atom catalyst (Pt_1/MnO_2) and Pt doped catalyst ($Pt\text{-}MnO_2$).
The texture and chemical properties of all catalysts were characterized by XRD, HAADF-STEM, STEM-EELS, XPS, Temperature programmed Toluene desorption (Toluene-TPD), Temperature programmed Toluene surface reaction (Toluene-TPSR). Catalytic performance was evaluated in a tubular reactor under atmospheric pressure. A reaction mixture of toluene (1000 ppm), O_2 (20%), and N_2 (balance) was continuously passed through the catalyst bed at a flow rate of 50 mL/min. The toluene concentration in the inlet and outlet gases was analysed using a gas chromatograph equipped with a FID detector.

3. Results and discussion

3.1 Chemical State and Electronic Properties

STEM-EELS measurements confirmed that a high proportion of low-valence Mn (Mn^{2+} and Mn^{3+}) exists at the interface between Pt and MnO_2. This indicates that charge transfer is occurring from Pt to MnO_2. The XPS spectrum confirmed that a large number of electrons were transferred to MnO_2 in the order of Pt-MnO_2, Pt_1/MnO_2, and Pt_{NPs}/MnO_2.

3.2 Catalytic Activity

The catalytic combustion curves of toluene over Pt/MnO_2 catalysts with different electronic properties are shown in Fig.1. The results show that nanoparticle Pt sites are more efficient than single-atom Pt sites. In the low-temperature combustion of toluene, electron-rich Pt species are effective, and it is thought that the overly strong EMSI effect reduces catalytic performance.

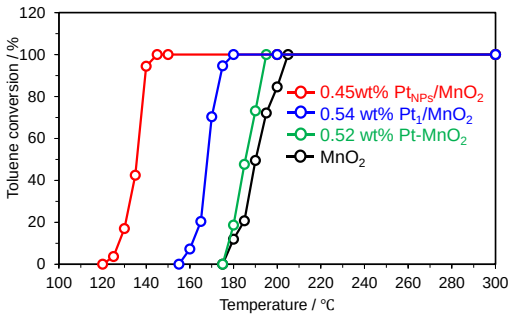

Fig.1 Catalytic performance Pt/MnO_2 catalysts

3.3 Reaction Mechanism

The CO_2 emission profiles for Toluene-TPD and Toluene-TPSR over Pt/MnO_2 catalysts are shown in Fig.2. Without oxygen, the surface lattice oxygen of the strong EMSI Pt_1/MnO_2 is most easily used for toluene combustion at low temperatures. This indicates that EMSI promotes the activation of surface lattice oxygen. However, with of oxygen, Pt_{NPs}/MnO_2, rather than Pt_1/MnO_2, is most easily used for toluene oxidation at low temperatures. This indicates that electron-rich Pt^0 species promote the activation of gas-phase oxygen.

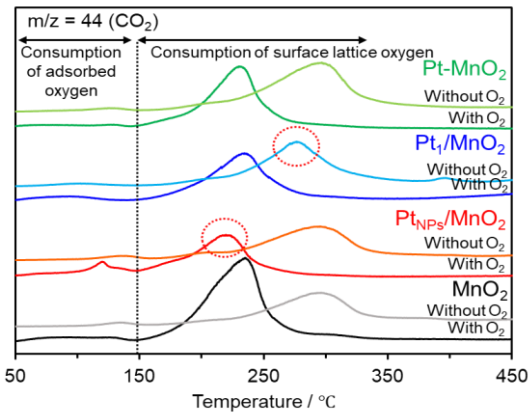

Fig.2 CO_2 emission profiles for Toluene-TPD and Toluene-TPSR over Pt/MnO_2 catalysts

4. Conclusions

STEM-EELS visualised the local electron transfer from Pt to MnO_2 in the Pt/MnO_2 catalyst. EMSI promotes the activation of surface lattice oxygen in MnO_2 at the interface with Pt. In addition, Electron-rich Pt^0 species promote the activation of gaseous oxygen. The Pt_{NPs}/MnO_2 catalyst, in which both surface lattice oxygen and gas-phase oxygen were activated by controlling the strength of EMSI appropriately, showed very high toluene combustion activity. This research clarified the relationship between EMSI and catalytic performance, and made a significant advance in understanding the reaction mechanism of toluene catalytic combustion.

References

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