

# Understanding the nature of manganese supported on activated carbon and its catalytic applications in aromatic alcohol oxidation

Tang Q. H.<sup>1,2</sup>, Chen Y. T.<sup>1</sup>, and Yang Y. H.<sup>1\*</sup>

<sup>1</sup>School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, 637459 (Singapore)

<sup>2</sup>Department of Chemistry, Henan Normal University, Xinxiang, 453007 (China)

\*yhyang@ntu.edu.sg

## Introduction

The development of effective heterogeneous catalysts for the oxidation of alcohols to the corresponding aldehydes or ketones using molecular O<sub>2</sub> as an oxidant is highly desired from a green chemistry point of view. Although many studies have been devoted to the aerobic oxidation of alcohols using supported or confined monomeric and nano-sized Ru-, Pd- or Au-based heterogeneous catalysts [1], it is still highly desirable to explore the use of inexpensive transition metal catalysts for the aerobic oxidation of alcohols because low catalytic activity gives more insight into the nature of active site and catalytic mechanism. It has been reported that an octahedral molecular sieve, synthetic manganese oxide materials with a channel structure, was an excellent catalyst to oxidize alcohols in the presence of molecular oxygen or air as the oxidant [2]. Herein, the superior catalytic performances of a carbon-supported K-Mn catalyst in the aerobic oxidation of aromatic alcohols is reported.

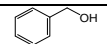

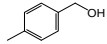

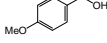

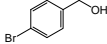

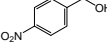

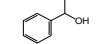

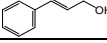

## Materials and Methods

The catalysts were prepared by co-impregnating aqueous solutions of potassium and manganese nitrates onto a commercially available activated carbon. The catalytic oxidation of alcohols was carried out with the following procedures. A certain amount of catalyst was added to a glass flask pre-charged with 2 mmol alcohol and 10 ml toluene, the mixture was heated to the desired reaction temperature under vigorous stirring. Then O<sub>2</sub> gas was bubbled into the mixture to start the reaction. After the reaction, the solid catalyst was filtered off and the liquid samples were analyzed by GC after adding an internal standard.

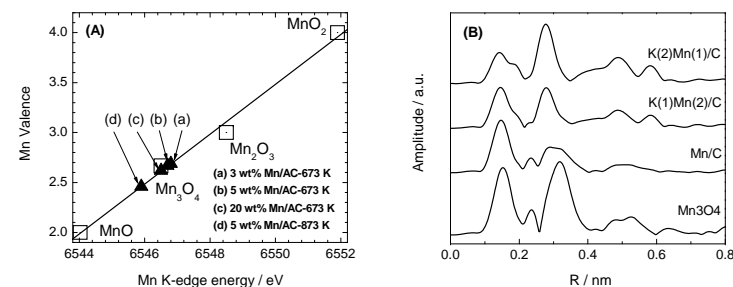
## Results and discussion

Manganese loading and treatment temperature were found to be vital factors in controlling the dispersion and chemical environment of activated carbon supported manganese oxides. Highly dispersed manganese oxides can be obtained with a Mn loading up to ca. 5 wt.% under modest pretreatment temperatures, whereas large amount of Mn resulted in aggregated MnO<sub>x</sub> crystalline clusters. The highly dispersed manganese oxides, uniformly distributed on activated carbon surface are mainly as coexistence of Mn<sup>2+</sup> and Mn<sup>3+</sup>. An improvement of the oxidation activity can be observed when the Mn/C catalyst is modified with potassium ions. Characterizations of XAFS evidence that potassium ions induce a large local distortion to Mn-O octahedrons in supported highly dispersed manganese oxides, which has been suggested to be a vital factor to enhance the activation of O<sub>2</sub> for the oxidation of aromatic alcohol. Moreover, a quantitative statistical model not only reveals the synergistic effects between reaction parameters, but also achieves a comprehensive understanding of the reaction process.

**Table 1. Catalytic properties of K(2)Mn(1)/C for oxidation of various alcohols with O<sub>2</sub><sup>a</sup>**

Substrate	Product	Time (h)	Conversion (%)	Selectivity (%)
		6	> 99	> 99
		6	> 99	> 99
		4	> 99	> 99
		8	97	> 99
		8	96	> 99
		24	74	> 99
		20	79	> 99

<sup>a</sup> Reaction conditions: the amount of catalyst, 0.2 g; reaction temperature, 373 K; substrate, 2 mmol; O<sub>2</sub> flow rate 10 cm<sup>3</sup>·min<sup>-1</sup>.



**Figure 1.** (A) Mn K-edge position of various Mn-containing catalysts along with reference compounds as a function of Mn valence; (B) Fourier transforms of Mn K-edge EXAFS for KMn/C (series phase shift was not corrected).

## Significance

The role of adding potassium is evidenced by XAFS to induce a large distortion of the Mn octahedral coordination with coexistence of Mn<sup>2+</sup> and Mn<sup>3+</sup>. A quantitative model achieves a comprehensive understanding of the reaction process of benzyl alcohol oxidation.

## References

- Hutchings G. J. *Chem Commun* 1148, (2008); Mallat T. and Baiker A. *Chem Rev* 3037, 104 (2004).
- Son Y.C., Makwana V. D., Howell, A. R., and Suib S. L. *Angew Chem Int Ed* 4280, 40 (2001).