## Manganese ions in-situ functionalized ZSM-5 for the catalytic oxidation of cyclohexane

X. R. Niu<sup>a</sup>, J. Li<sup>a</sup>, L. Zhang<sup>a</sup>, Z. T. Lei<sup>a,b</sup>, X. L. Zhao<sup>a</sup> and C. H. Yang<sup>\*a,b</sup>

<sup>a</sup>MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering & Key Laboratory of Micro-systems and Micro-structures, Ministry of Education, Harbin Institute of Technology, 150001 Harbin, People's Republic of China. E-mail: yangchh@hit.edu.cn

<sup>b</sup> Key Laboratory of Micro-systems and Micro-structures Manufacturing of Ministry of Education, Harbin Institute of Technology, Harbin 150001, China.



Fig. S1 SEM of P3 sample used for EDS Mapping shown in fig. 3



Fig. S2 SEM of P<sub>3</sub> sample after six times catalytic reaction and corresponding EDS mapping: Si (blue-green), Al (yellow), O (green) and Mn (purple)

sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Mn/(Mn+Si)
reaction mixture		
P <sub>3</sub> after 6 times usage	50	1.30



**Fig. S3** GC curve of the catalytic products by 2% Mn-ZSM-5, the peaks in different times correspond to different products: 1.340 min (cyclohexane), 2.033 min (acetonitrile), 8.705 min

(cyclohexanone) and 9.773 min (cyclohexanol)

The gas chromatogram (GC) curve was drawing out with concentration of the components from the end of the column plotted against the time after injection. Time at 2.033 is corresponding to acetonitrile functioned as solvent, which is a main component among the product mixture. Cyclohexanone at 8.705 min and cyclohexanol at 9.773 min are the whole composition of the catalytic oxidation of cyclohexane at 1.340 min.



Fig. S4 FTIR spectra of the P<sub>3</sub> sample after five times usage without(a) and with(b) calcination.