Electronic Supplementary Material (ESI) for RSC Advances

Nano-Layered Manganese Oxides as Low-Cost, Easily Synthesized, Environmentally Friendly and Efficient Catalysts for Epoxidation of Olefins

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Materials and Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1}. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H_2O_2, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS. The products of oxidation reactions were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m · 320 lm · 0.25 lm) and flame-ionization detector.

Synthesis of compounds

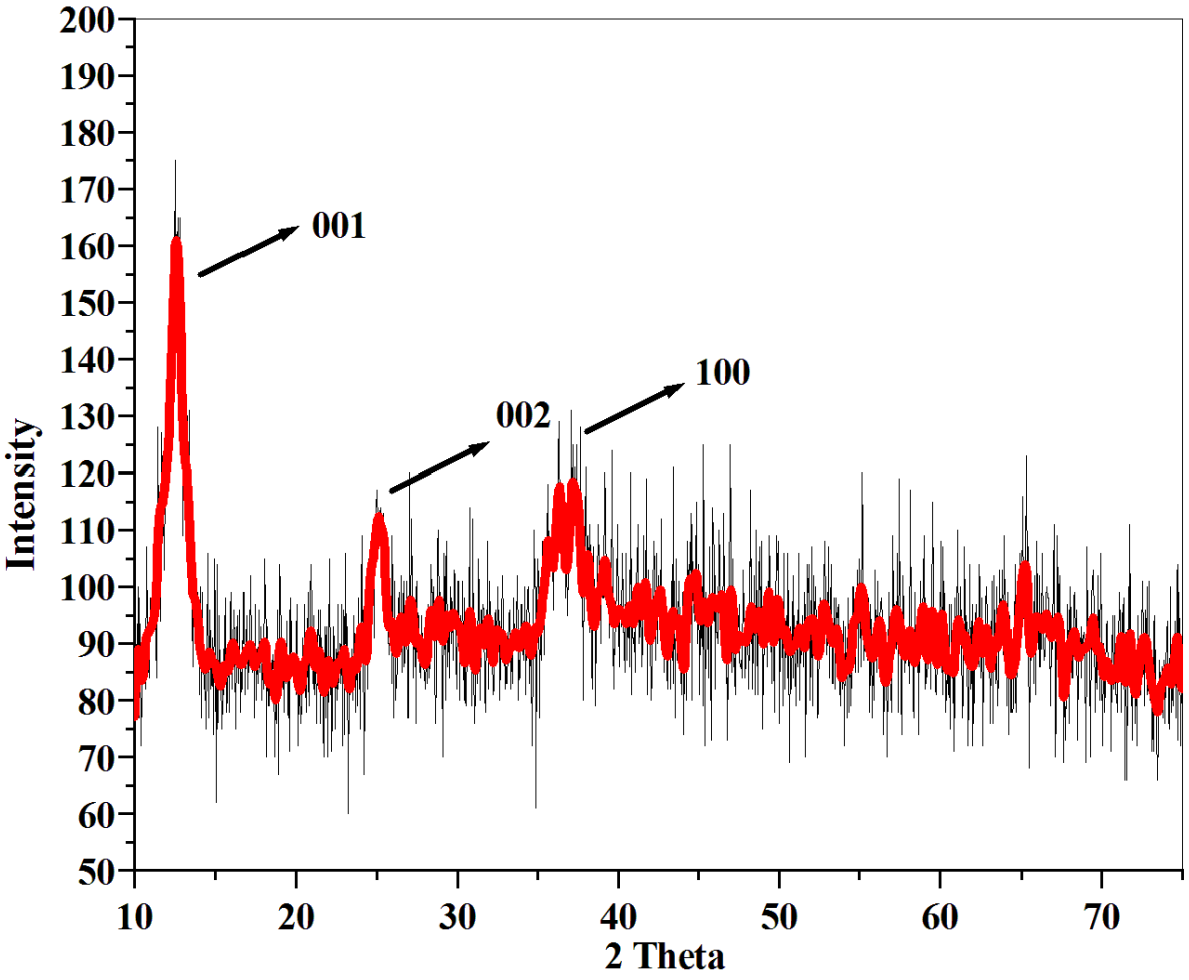
Different conditions were used to obtain the catalysts for water oxidation but the best catalyst was synthesized using the below condition:

Solution **1**: $CaCl_2.4H_2O$ ($AlCl_3$ or $Zn(CH_3COO)_2$) (4.0 mmol) and $Mn(CH_3COO)_2.4H_2O$ (5.6 mmol, 1372 mg) were dissolved in water (5 mL). The mixture was stirred for about 10 min. at room temperature.

Solution **2**: to a solution of $KMnO_4$ (2.4 mmol, 379 mg) in 60 mL water, KOH was added to obtain a hot saturated KOH solution.

Addition of solution **1** to solution **2** under vigorous stirring resulted in a dark precipitate. Then the mixture was allowed to cool with continued stirring for 2 h.

The obtained suspension was filtered and washed using distilled water (3L) before being allowed to dry for 12 h at 60°C in an oven. Then the solid was heated to 400°C for 10 h in air to obtain a black powder. Yield: (~%99).



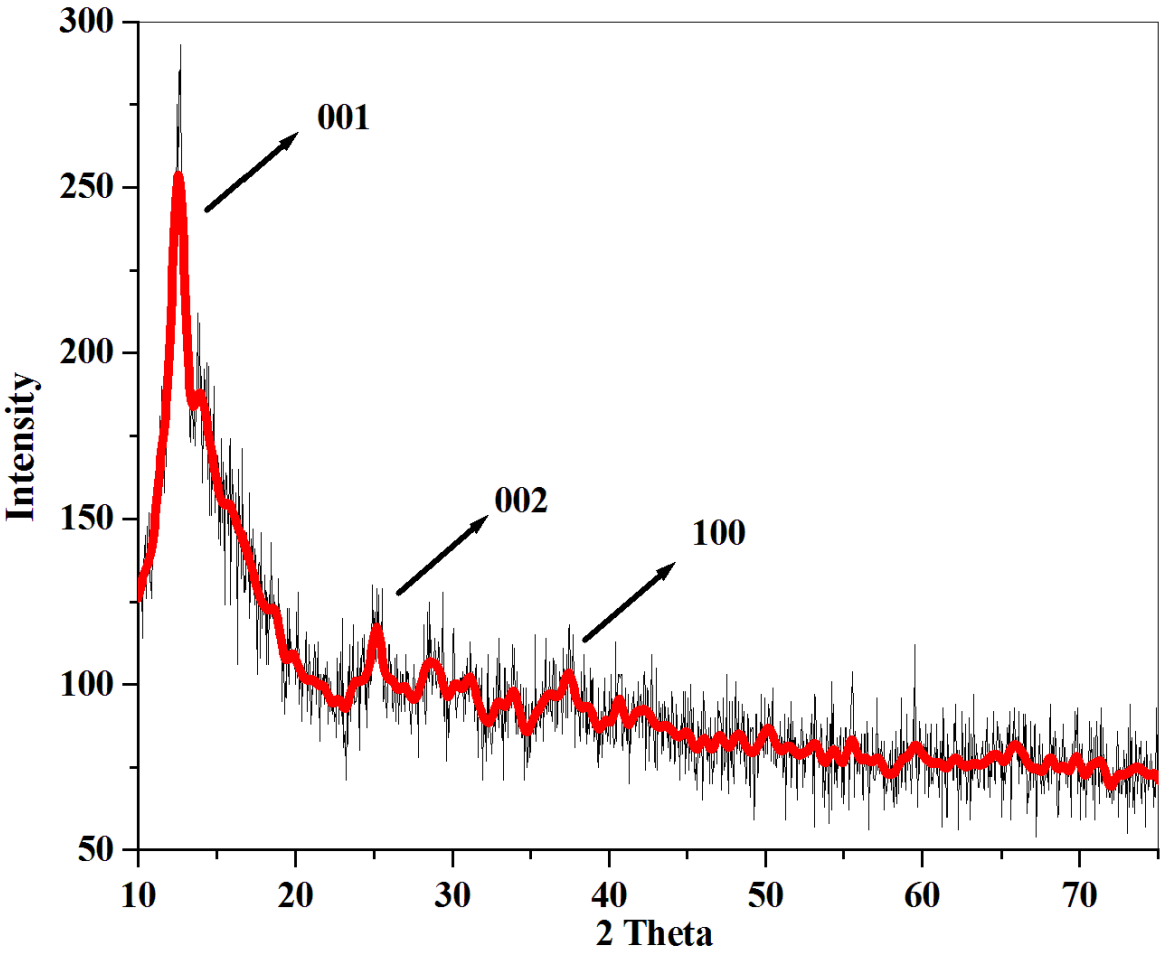
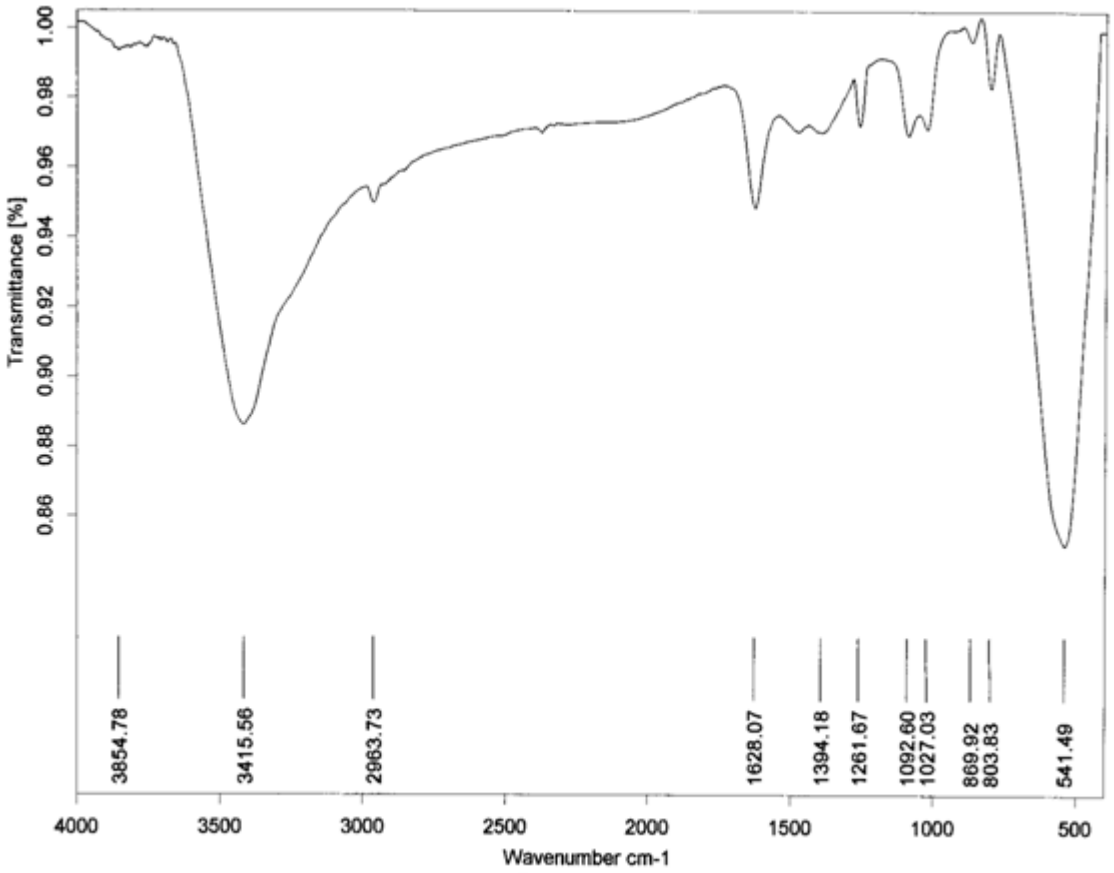
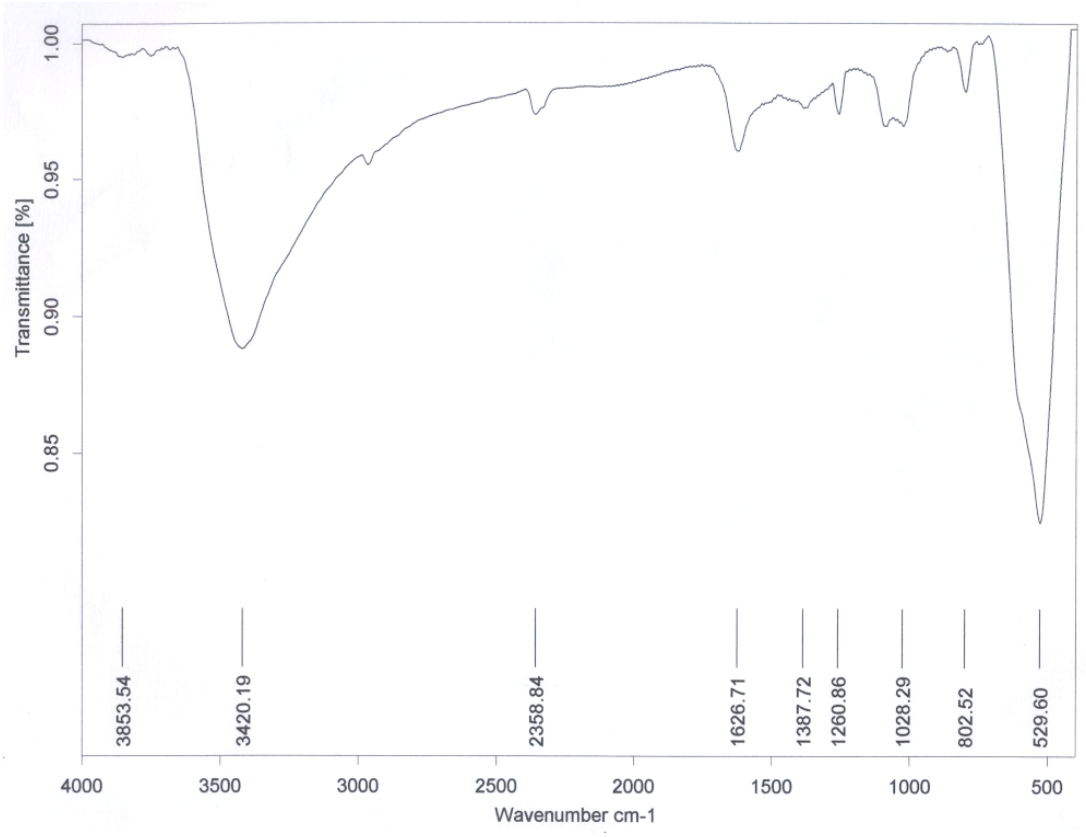


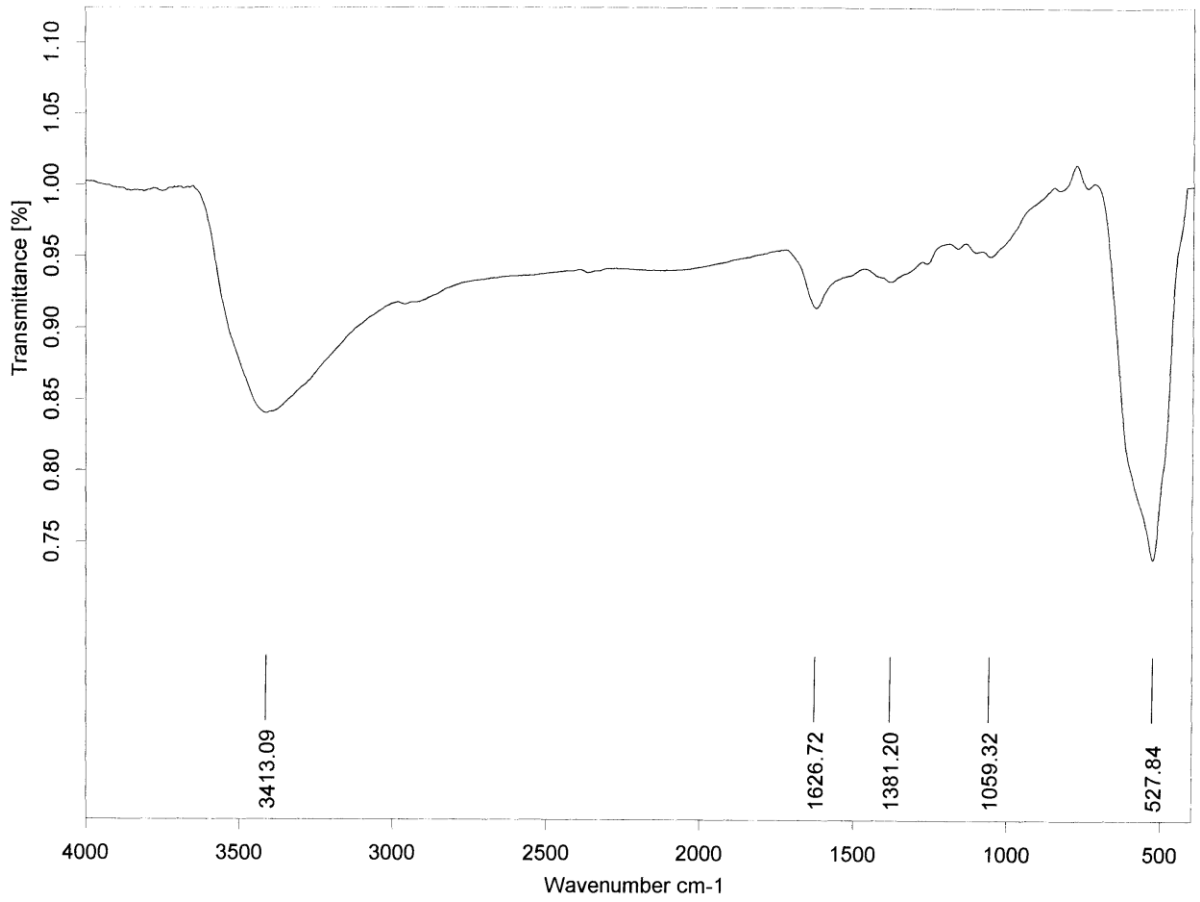
Fig. 1S XRD patterns of the obtained of zinc - manganese oxide (top) and aluminium - manganese oxide (below) and FFT Filter Smoothing of XRD patterns of these compounds (red) (Below).



(a)



(b)



(c)

Fig. 2S**.** IR spectra of the calcium (a), zinc (b) and aluminium - manganese oxides (c). A broad band at ~ 3200-3500 cm^{-1} is related to antisymmetric and symmetric O-H stretchings and at ~ 1630 cm^{-1} related to H-O-H bending are observed. A band at ~ 520-540 cm^{-1} is attributed to υ_{Mn-O} stretching vibration of Mn-O bonds.[1]

References:

1. Y. Chen, Y. Zhang, Q.Z. Yao, G.T. Zhou, S. Fu, H. Fan, *J. Solid State Chem*., 2007, **180**, 1218.