Supplementary data

A non-nitric acid method of adipic acid synthesis: organic solvent- and promotor-free oxidation of cyclohexanone with oxygen over hollow-structured Mn/TS-1 catalysts

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Table S1 Comparison between the novel catalyst and the others reported previously.

Catalyst	Conv.	AA Sele.	Oxidant	Temp.	Solvent	Reference
Mn-HTS	68.4	93.1	O_2	90	No	This work
Pt/Carbon/monolith	100	22	O_2	140	Water	[1]
Pt/Carbon	100	38.8	O_2	140	Acetic acid/water	[2]
$Mn(OAc)_2$	99.8	75	O_2	65	Acetic acid/CF_3COOH	[3]
$Mn(NO_3)_2/Co(NO_3)_2$	97.5	93.4	O_2	40	Acetic acid/HNO_3	[4]
Co/Mn cluster	97.6	86.6	O_2	100	Acetic acid/water	[5]
$H_5PMo_{10}V_2O_{40}$	99	51	O_2	70	Acetic acid/water	[6]
$H_7PMo_8V_4O_{40}$	98	55	O_2	60	Acetonitrile/methanol	[7]

[1] E. Crezee, F. Kapteijn and J. A. Moulijn, *Catal. Today*, 2001, 69, 283–290.
[2] M. Besson, F. Gauthard, B. Horvath and P. Gallezot, *J. Phys. Chem. B*, 2005, 109, 2461-2467
[3] M. Constantini and L. Krumenacker, *FR Patent* 2541993, 1983 (patent held by Rhone Poulenc).
[4] C. Fumagalli, F. Minisci and R. Pirola, *WO Patent* 01/87815, 2001 (patent held by Lonza SpA).
[5] S. A. Chavan, D. Srinivas and P. Ratnasamy, *J. Catal.* 2002, **212**, 39–45.
[6] A. Atlamsani, J.-M. Brégeault and M. Ziyad, *J. Org. Chem.*, 1993, **58**, 5663–5665.
[7] J.M. Brégeault, E.A. Bassam and J. Martin, *US Patent* 4983767, 1991 (patent held by Rhone Poulenc Chimie).

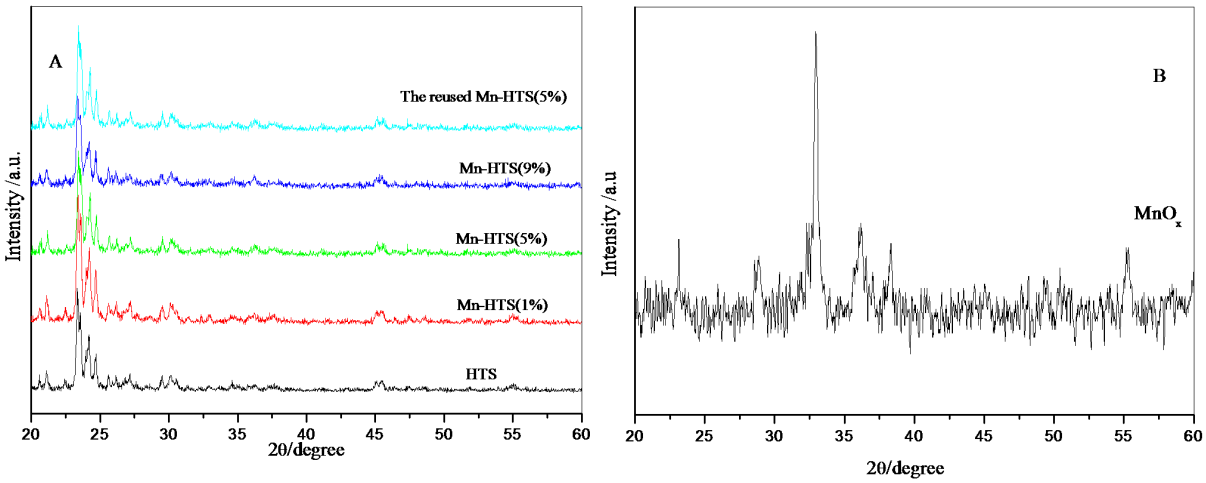

Fig. S1 XRD of samples parent HTS, the xMn-HTS, the reused Mn-HTS(5%) (A) and MnO_x (B)

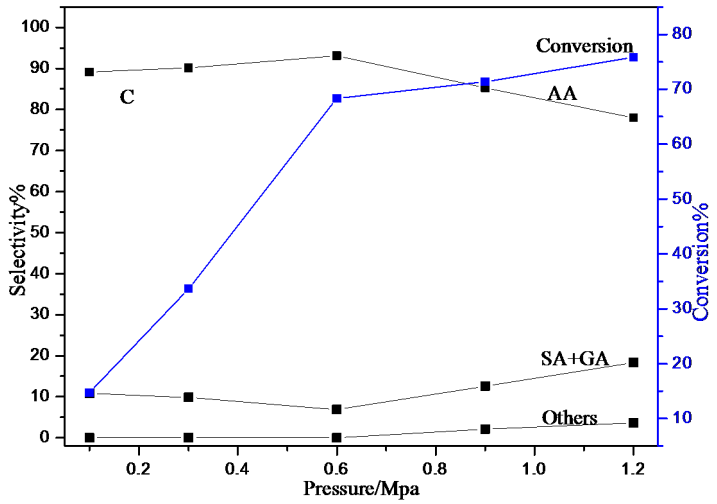

Fig. S2 Effect of the reaction pressure on the conversion of cyclohexanone and AA selectivity over the synthesized 5% Mn-HTS. (reaction conditions: 40 g cyclohexanone; GA+SA: glutarate acid and succinate acid; Others include CO_2 and CO).

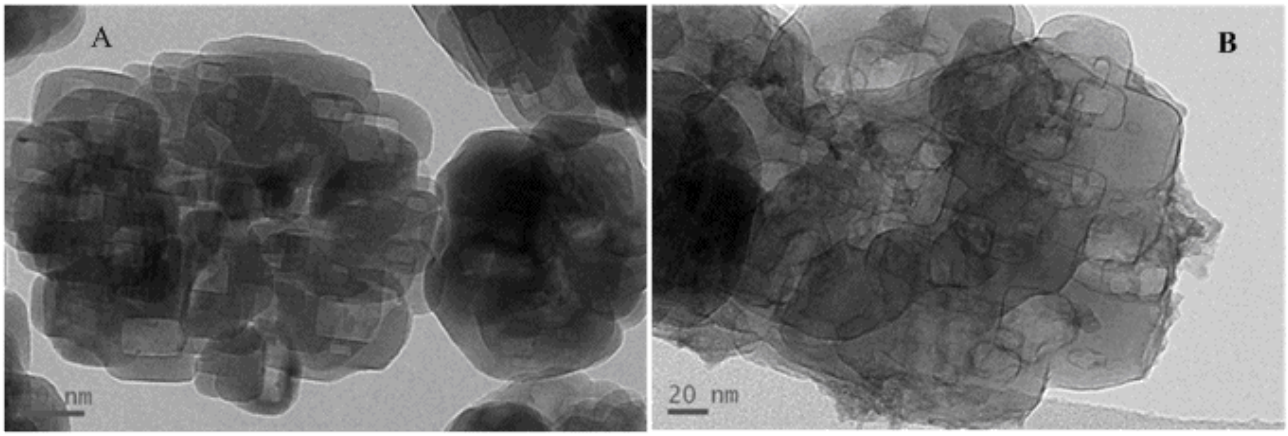

Fig. S3 TEM images of the reused Mn-HTS(5%)

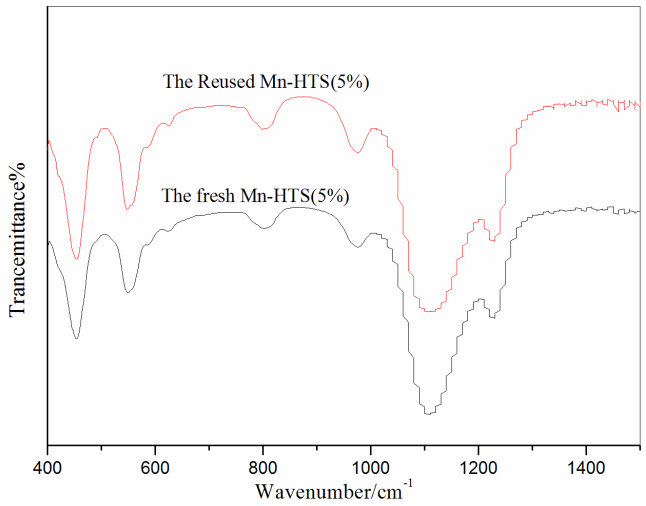

Fig. S4 FT-IR spectra of the fresh Mn-HTS (5%) and the reused Mn-HTS(5%)