Facile synthesis of Mn-Fe/CeO_2 nanotubes by gradient electrospinning and their excellent catalytic performances for propane and methane oxidation

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Experimental

Characterizations

X-ray diffraction (XRD) patterns were conducted on a RIGAKU-Miniflex II X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å). N_2 physisorption measurement was performed on an ASAP 2020 apparatus. Field Emission Scanning Electron Microscope (FE-SEM) was carried out on JSM6700-F. Transmission electron microscopy (TEM) measurements were carried out on a JEM-2010 microscope operating at 200 kV with an energy dispersive X-ray spectroscopy (EDX) detector. The preparation of samples for analysis involved being ultrasonically dispersed in absolute ethanol and deposition on a carbon-Cu grid. Thermal analysis (TGA) of the sample was performed using a STA449C apparatus (NETZSCH). Samples of about 10 mg were loaded into an alumina pan, then heated from 25 to 800 ^oC at a rate of 10 ^oC/min. All measurements were conducted under air. Atomic force microscopy (AFM) imaging was done using Bruker Dimension ICON AFM. The AFM imaging was done by drop-casting the methanolic dispersions of the LDHs on silicon wafers followed by drying and incubation for 12 h. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out using an Ultima2 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted on Physical Electronics Quantum 2000, equipped with a monochromatic Al-K_α source (K_α = 1,486.6 eV) and a charge neutralizer. Raman spectra of samples were recorded at ambient condition on a Renishaw spectrometer, and a laser beam (λ= 532 nm) was used for the excitation. H_2

temperature-programmed reduction (H_2-TPR) was performed on a Micromeritics AutoChem II 2920 equipped with a TCD detector, in which the catalysts was pre-treated under air flow (30 mL/min) at 400 °C for 0.5 h, purged with Ar (30 mL/min) for 0.5 h and then naturally cooled down to ambient temperature. H_2-TPR measurement was recorded from 50 to 800 °C under 10 vol% H_2/Ar. Oxygen temperature-programmed desorption (O_2-TPD) was carried out on an AutoChem 2920 equipped with a TCD detector. The sample was heated to 900 °C at a rate of 1 °C/min in a pure He gas flow and the signals for O_2 (m/z = 32), H_2O (m/z= 18), and CO_2 (m/z=44) were detected online by using a Hiden QIC-20 quadruple mass spectroscopy (Q-MS).

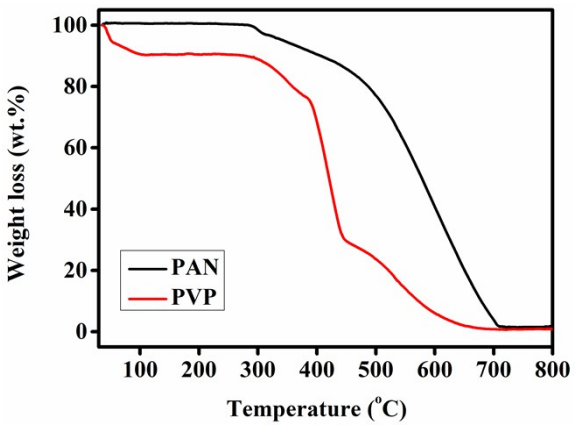

Figure S1 TGA weight percentage versus temperature curves for PAN and PVP.

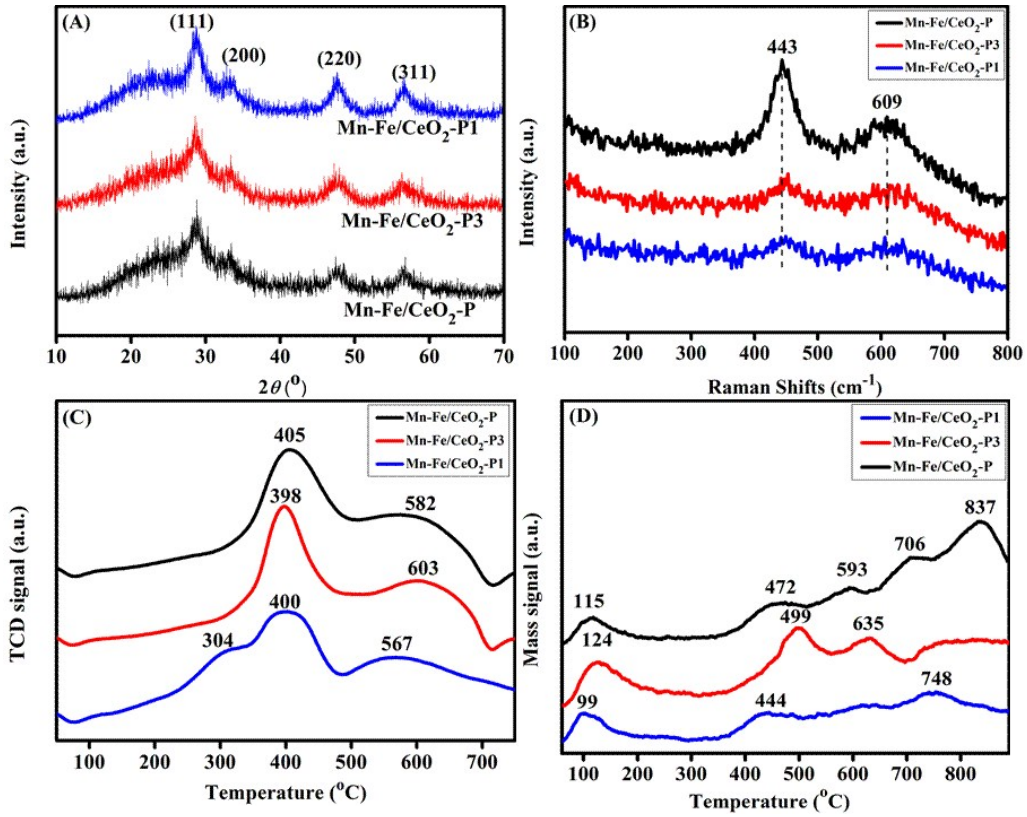

Figure S2 (A) XRD patterns; (B) Raman spectra; (C) H_2-TPR profiles and (D) O_2-TPD-MS of Mn-Fe/CeO_2-P, Mn-Fe/CeO_2-P1 and Mn-Fe/CeO_2-P3 catalysts.

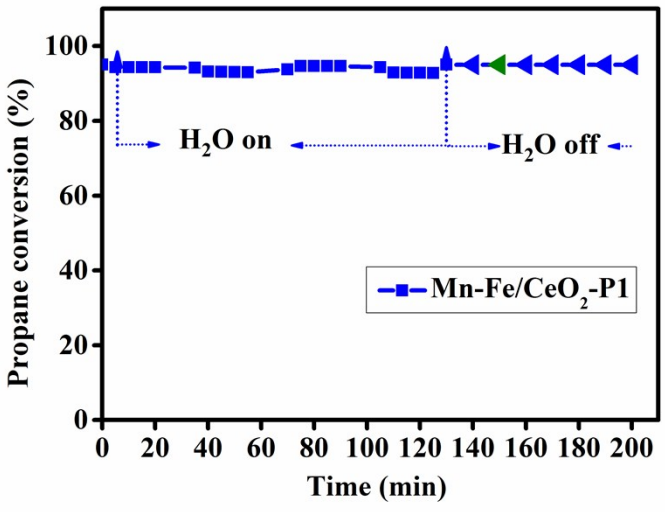

Figure S3 Water-resistant performance of Mn-Fe/CeO_2-P1 at 400 °C

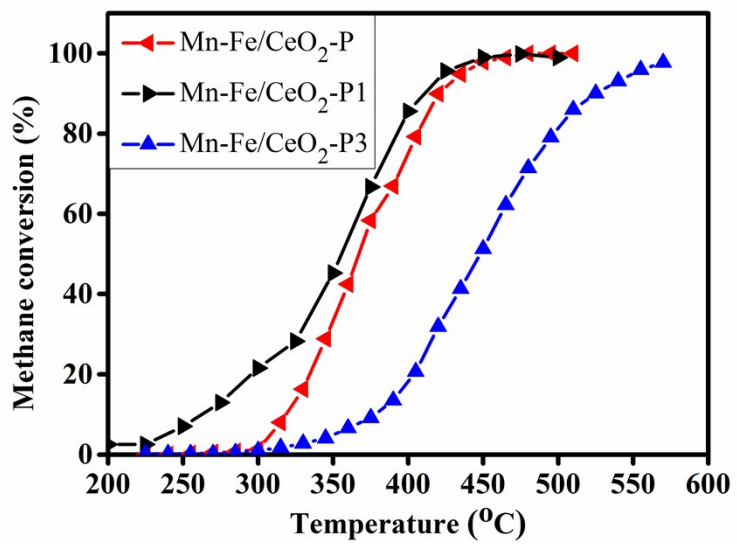

Figure S4 Methane conversion of Mn-Fe/CeO_2 catalysts.

Table S1 ICP results of as-prepared Mn-Fe/CeO_2 catalysts.

Sample	Mn content (wt.%)	Fe content (wt.%)	Ce content (wt.%)
Mn-Fe/CeO_2-P	8.51	8.81	44.70
Mn-Fe/CeO_2-P1	8.39	8.74	43.84
Mn-Fe/CeO_2-P3	8.71	8.96	45.11

Table S2. BET surface area, reaction temperature, surface atomic concentration, Mn^{4+}/Mn^{3+}, $Ce^{3+}/(Ce^{4+}+Ce^{3+})$ and $O_{ads}/(O_{ads}+O_{latt})$ molar ratios.

Sample	S_{BET} (m^2/g)	T_{50} % (°C)	$T_{90\%}$ (°C)	Surface atomic concentration by XPS (%)				Relative molar ratios by XPS (%)		
				Mn	Fe	Ce	O	$Mn^{4+}/(Mn^{3+}+Mn^{4+})$	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$	$O_{ads}/(O_{ads}+O_{latt})$
Mn-Fe/CeO_2-P	100	339	-	5.15	6.31	8.55	50.91	45	25	46
Mn-Fe/CeO_2-P1	89	318	382	4.51	5.85	8.79	51.58	45	27	51
Mn-Fe/CeO_2-P3	96	398	-	3.32	7.12	7.12	49.55	46	27	46