Supporting Information

An enhanced selective hydrogenation performance of methyl benzoate and impacts promoted by Al-modified KMn/SiO_2

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Experimental Section

Materials and Methods

Materials

All chemical materials for preparing corresponding catalysts were used as purchased without further purification. Manganese (II) nitrate 50% water solution (analytical reagent, Shanghai Macklin Biochemical Technology Co., Ltd), Aluminium nitrate nonahydrate (Al(NO3)3·9H2O, analytical reagent, Shanghai Aladdin Biochemical Technology Co., Ltd), Potassium nitrate (KNO3, analytical reagent, Shanghai Lingfeng Chemical Reagent Co., Ltd), Silicon dioxide (SiO2, Q10, Fuji Sylysia Chemical Ltd), Methyl benzoate (C8H8O2, analytical reagent, Shanghai Aladdin Biochemical Technology Co., Ltd).

Catalyst characterization

The crystal phase in the catalysts was analyzed by a Rigaku Ultima IV X-ray diffractometer (XRD) from Rigaku corporation, with Cu Kα radiation source ((λ = 0.154 nm). The scanning step size was 0.04° and the scanning range was 2θ = 5–80°. The N_2 physical adsorption-desorption analysis of the catalyst was performed using a Microtrac BELSORP-mini II fully automatic physical adsorption instrument to determine the porous structure in the catalysts. The surface element and valence state of the catalyst were investigated by a Thermo Scientific ESCALAB 250XI X-ray photoelectron spectrometer (XPS) from Thermo Fisher. Additionally, H2-TPR, H2-TPD, and NH3-TPD experiments were carried out on the catalyst using a BELCAT-B3 fully automatic three-station chemical adsorption instrument from Microtrac BELSORP-mini II in Japan. Finally, thermogravimetric analysis of the catalyst was conducted utilizing a Netzsch STA449F3 synchronous thermal analysis tester. The loadings of catalysts were determined using the inductive coupling plasma atomic emission spectroscopy (ICP-AES) over a Varian ICP-OES-720 instrument. In the sample preparation, the Co portion was dissolved from catalyst powder by aqua regia. The resulting solution was then diluted to the desirable concentration for further measurement. The scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDX) investigations were carried out with a Hitachi FESEM SU8220 electron microscope.

Table S1 Surface Area and Pore Properties of the Catalysts

Samples	S_{BET} ($m^2 \cdot g^{-1}$)[a]	V_p ($cm^3 \cdot g^{-1}$)[b]	Pore size (nm)[c]
SiO_2	258	0.98	15.2
KMn/SiO_2	63	0.53	34.3
KMn/SiO_2-1%Al	69	0.45	26.7
KMn/SiO_2-3%Al	74	0.42	23.8
KMn/SiO_2-5%Al	78	0.46	24.5
KMn/SiO_2-10%Al	80	0.39	19.9

[a]Total surface area evaluated by BET method; [b]Total pore volume adsorbed at P/P0=0.99; [c]Average pore diameter

Table S2 H_2 desorption amounts in different temperature regions of the prepared catalysts

Catalysts	Low temperature（mmol·g^{-1}）	High temperature（mmol·g^{-1}）
KMn/SiO_2	0.022	0.050
KMn/SiO_2-1%Al	0.030	0.052
KMn/SiO_2-3%Al	0.033	0.051
KMn/SiO_2-5%Al	0.037	0.068
KMn/SiO_2-10%Al	0.047	0.084

Table S3. The total desorption amount of the catalyst NH_3 in the NH_3-TPD test

Catalyst(fresh)	Total desorption amount of NH_3 (mmol/g)
KMn/SiO_2	0.232
KMn/SiO_2-1%Al	0.101
KMn/SiO_2-3%Al	0.104
KMn/SiO_2-5%Al	0.208
KMn/SiO_2-10%Al	0.380

Table S4 Proportion of different O species on the catalyst surface before and after the reaction

Catalyst(fresh)	O_{ads}		O_{Si-O}		O_{H2O}	
	Peak(eV)	%	Peak(eV)	%	Peak(eV)	%
KMn/SiO_2	530.9	24.7	532.6	71.7	534.2	3.6
KMn/SiO_2-1%Al	531.2	25.1	532.6	70.9	534.3	4.0
KMn/SiO_2-3%Al	531.0	30.4	532.3	66.1	534.0	3.5
KMn/SiO_2-5%Al	531.3	39.3	532.4	56.7	534.0	4.0

KMn/SiO_2-10%Al	531.0	54.7	532.1	42.0	533.6	3.3

Catalyst(spent)	O_{ads}		O_{Si-O}		O_{H2O}	
	Peak(eV)	%	Peak(eV)	%	Peak(eV)	%
KMn/SiO_2	530.9	20.3	532.8	77.7	534.9	2.0
KMn/SiO_2-1%Al	531.2	21.2	533.0	76.8	535.1	2.0
KMn/SiO_2-3%Al	513.6	28.9	533.1	68.1	534.8	3.0
KMn/SiO_2-5%Al	532.2	52.2	533.3	45.1	534.9	2.7
KMn/SiO_2-10%Al	531.9	54.3	533.2	42.7	534.5	3.0

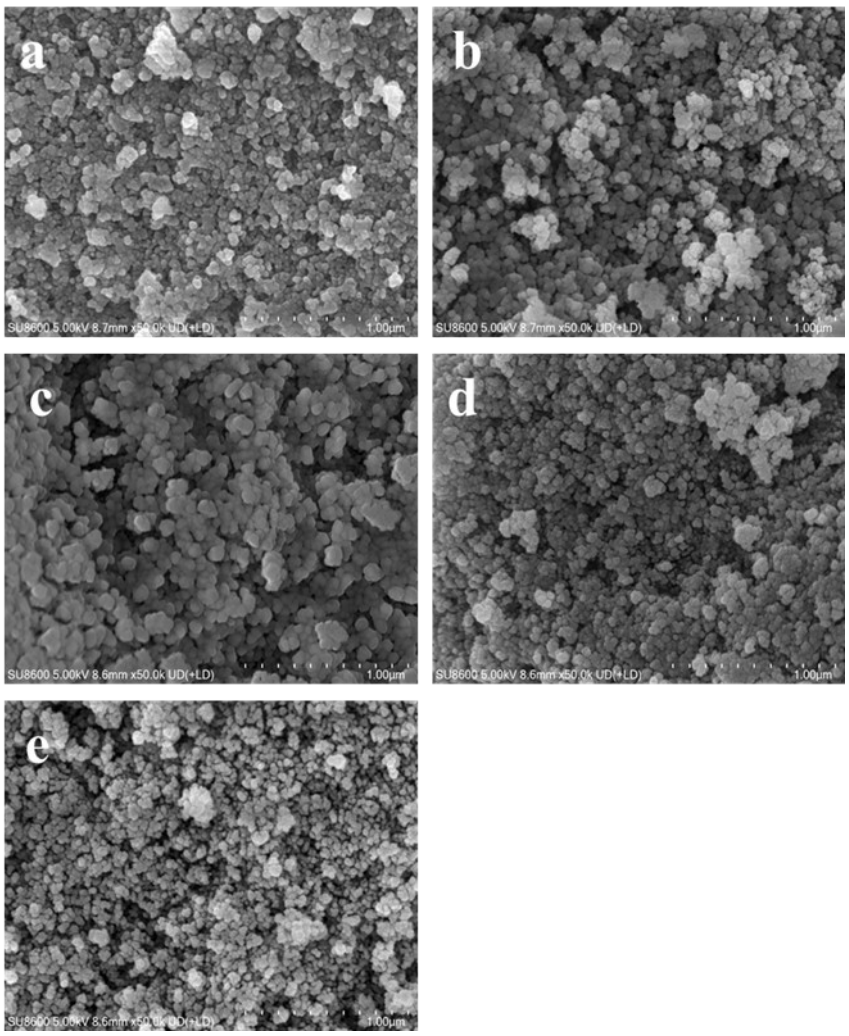

Fig. S1 SEM images of the fresh catalysts. a-e, (**a**) KMn/SiO2; (**b**) KMn/SiO2-1%Al; (**c**) KMn/SiO2-3%Al; (**d**) KMn/SiO2-5%Al; (**e**) KMn/SiO2-10%Al.

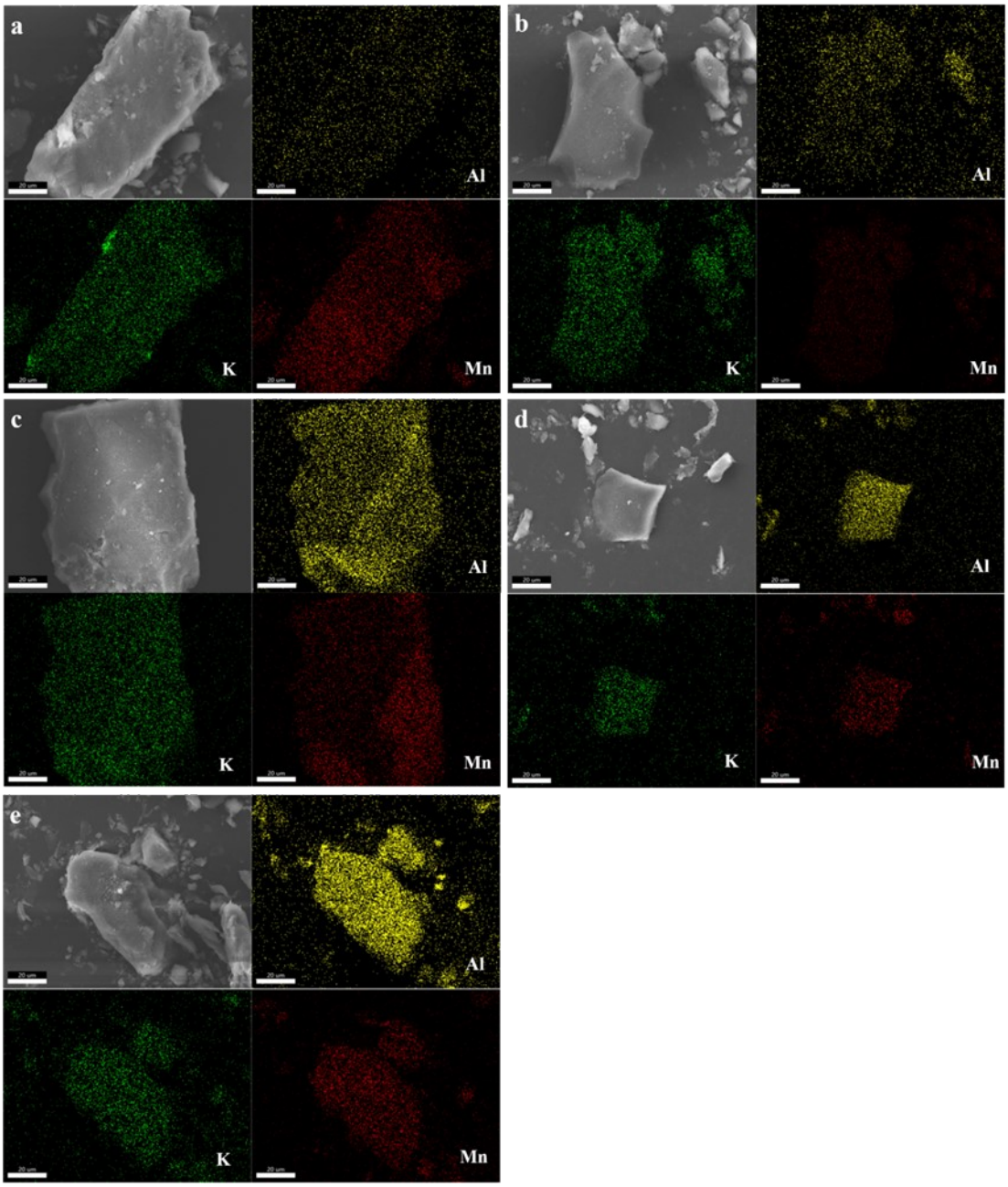

Fig. S2 SEM images and corresponding EDS mapping patterns showing the distribution of Al (yellow), K (green) and Mn (red) in selected areas of catalysts with different Al contents. a-e, (**a**) KMn/SiO2; (**b**) KMn/SiO2-1%Al; (**c**) KMn/SiO2-3%Al; (**d**) KMn/SiO2-5%Al; (**e**) KMn/SiO2-10%Al.

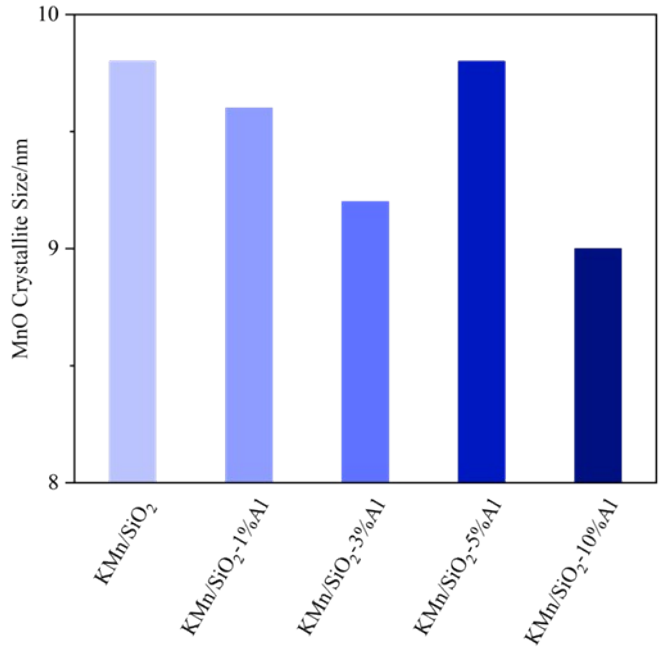

Fig. S3 MnO crystallite sizes of the catalysts after reduction.

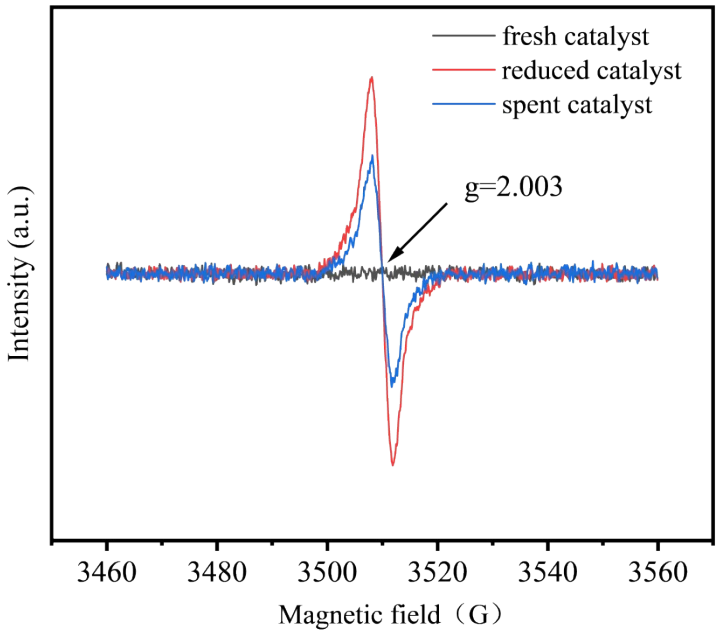

Fig. S4 EPR spectra of KMn/SiO2-5%Al catalysts with different treatments

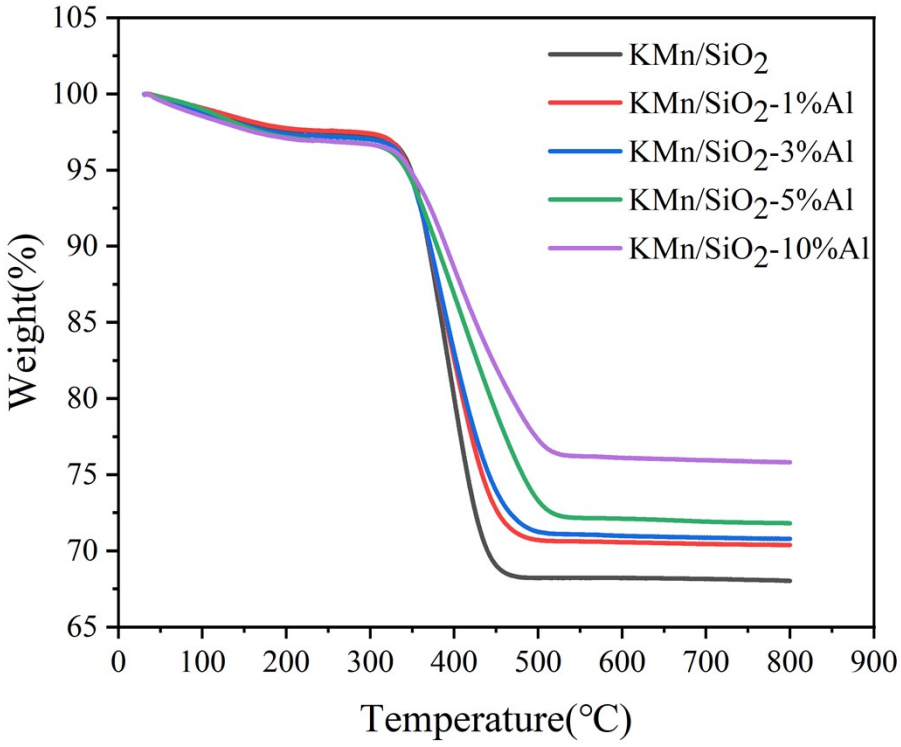

Fig. S5 TG profiles of KMn/SiO_2-Al catalysts after reaction