Supplementary Information

Manganese oxide as an alternative to vanadium-based catalysts for effective conversion of glucose to formic acid in water

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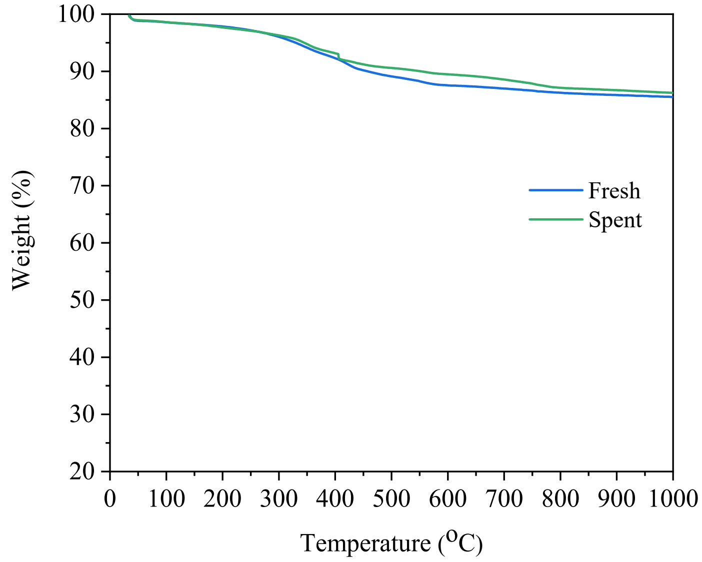

Figure S1 Thermal gravimetric analyses (TGA) of fresh MnO_x-100 and spent MnO_x-100 after reaction at 170 °C for 150 min.

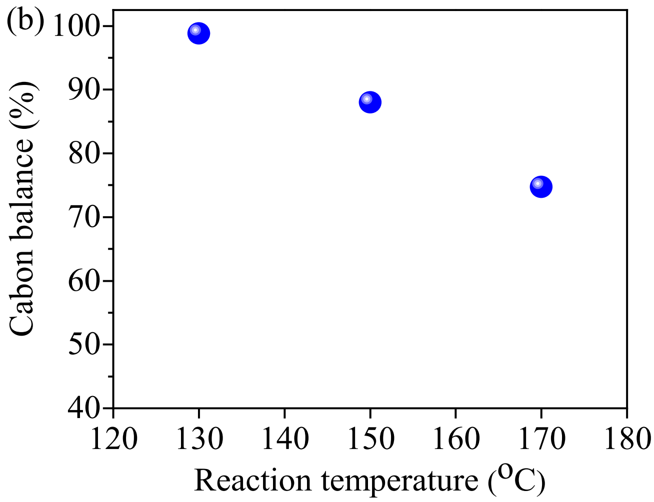

Figure S2 Carbon balances obtained after oxidation reaction with MnO_x-100 catalyst at several temperatures. Reaction conditions: 50 mg catalyst, 100 mg glucose, 5 mL H_2O, 150 min reaction time, 3 MPa O_2

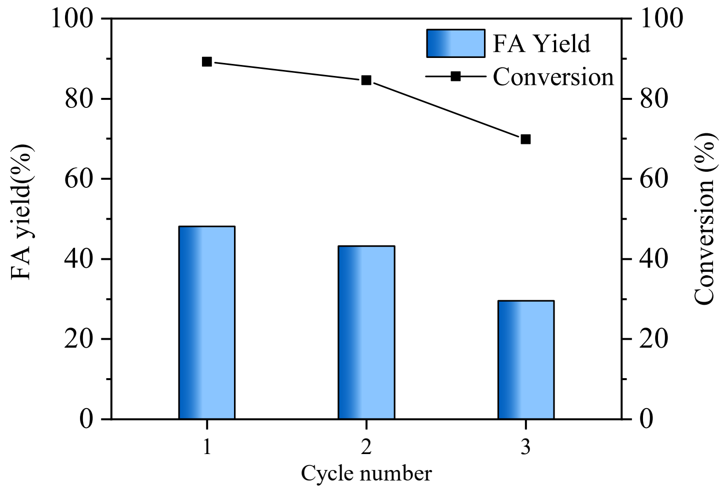

Figure S3 Recyclability of MnO_x-100 catalyst for initial catalyst dosage of 50 mg. Reaction conditions: 100 mg glucose, 5 mL H_2O, 150 ^oC, 3 MPa O_2, 100 min reaction time.

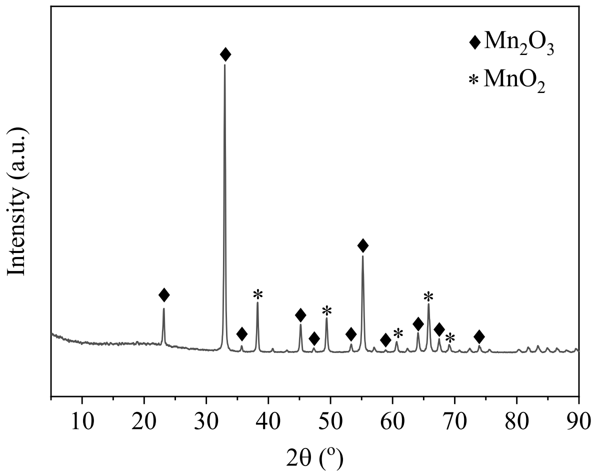

Figure S4 XRD spectrum of MnO_x-100 catalyst after three cycles of use according to conditions in Fig. S3. (MnO_2: JCPDS PDF# 72-1982. Mn_2O_3: JCPDS PDF# 41-1442)

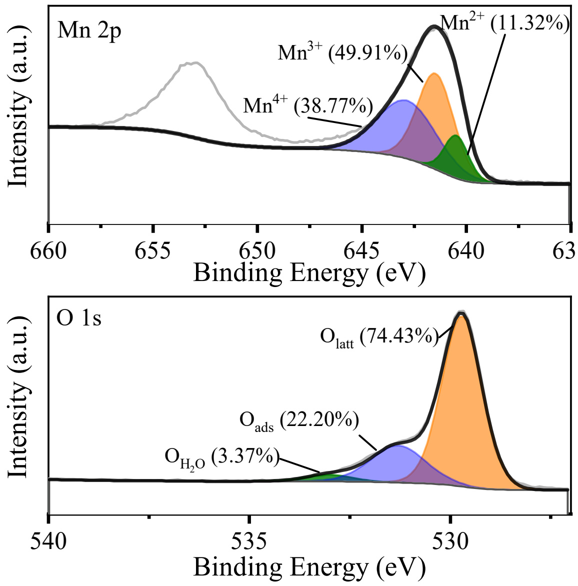

Figure S5 XPS of spectrum of MnO_x-100 catalyst after three cycles of use according to conditions in Fig. S3

Table S1 Total surface area and pore volume of synthesized catalysts

Catalyst	$S_{BET}(m^2 \cdot g^{-1})$	Pore volume ($cm^3 \cdot g^{-1}$)
MnO_x-100	28.0	0.30
MnO_x-120	16.7	0.08
MnO_x-140	16.9	0.08

Table S2 Comparison of maximum formic acid (FA) yields obtained from glucose in aqueous solutions for different homogeneous catalysts

Catalyst	Key reaction conditions				Yield (%)	Ref.
	Glucose concentration (g/L)	Oxidant concentration or O_2 partial pressure	Temperature (°C)	Time (h)		
LiOH	9	2.5 mmol H_2O_2	35	8	91.3	1
KOH	-	1 mmol H_2O_2	250	1/60	75.0	2
NaOH	-	1 mmol H_2O_2	259	1/60	70.0	2
$VOSO_4$	9	2 MPa O_2	140	1	45.0	3
$FeCl_3$+ H_2SO_4	26	3 MPa O_2	170	5/6	52.3	4
$NaVO_3$+H_2SO_4	17	3 MPa O_2	160	1/60	68.2	5
$H_4PVMo_{11}O_{40}$	10	2 MPa O_2	180	3	54.5	6
$H_5PV_2Mo_10O_{40}$	10	2 MPa O_2	100	3	55.0	7
$H_6PV_3Mo_9O_{40}$	50	3 MPa O_2	90	8	56.0	8
$H_7PV_4Mo_8O_{40}$	50	3 MPa O_2	90	8	52.0	8
$H_7PV_5Mo_8O_{40}$	22	6 MPa O_2	80	8	58.2	9

Table S3 Conversion of glucose, arabinose or glyoxylic acid to formic acid (FA) with MnO_x-100 catalyst. Reaction conditions: 50 mg catalyst, 20 g/L substrate, 5 mL H_2O, 160 °C, 3 MPa O_2, 100 min reaction time.

Substrate	Conversion (%)	FA yield (%)
Glucose	94.6	55.7
Arabinose	100	69.8
Glyoxylic acid	100	73.4

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