

Supporting Information

Selective Oxidation of Glycerol to Tartronic Acid over Pt/N-doped Mesoporous Carbon with Extra Framework Magnesium Catalysts under Base-Free Condition

KEYWORDS: Extra framework Magnesium, N-doped mesoporous carbon, Pt, glycerol oxidation, tartronic acid

2. Experimental Section

2.1 Catalyst preparation

The resol precursor was prepared according to the procedure in the literature.¹ MgO doped NMC were first synthesized based on a modified procedure reported in a previous study.² Briefly, 1.0 g F127 and 2.0 g of dicyandiamide (DCDA) were first dissolved in a mixture of ethanol (20.0 g) and water (10.0 g). Then, a certain amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was added into the above solution, after 5.0 g of resol ethanol solution (20 wt%) was added, pH value was adjusted to 4.0 by dropping 0.5 mol/L HNO_3 and further stirred for 0.5 h. Transparent composite films were obtained by pouring the solution into Petri dishes to evaporate the solvent at 50 °C for 6 h. After further heating in an oven at 100 °C for 24 h for thermosetting, the as-made composites were scrapped and crushed into powders for pyrolysis. The pyrolysis was carried out in a tubular furnace under N_2 atmosphere at 350 °C for 3h with a ramp rate of 1 °C min^{-1} and then 1000 °C for 1h with a ramp rate of 3 °C min^{-1} . The as calcined samples are designated as MgO-NMC-X, where X is the weight percentage of $\text{Mg}(\text{NO}_3)_2$ to F127, DCDA and resol. For the purpose of comparison, mesoporous carbon materials are also prepared according to the above method, which are denoted as MC.

For the synthesis of NMC with extra framework magnesium, the MgO-NMC-X samples (0.5 g) were stirred in 50 mL 1 mol/L HNO_3 solution for 24 h at room temperature, followed by washing with copious water until pH is neutral, then dried in 110 °C oven. The obtained samples are designated as Mg-NMC-X (Mg-NMC-5%, Mg-NMC-10% and Mg-NMC-15%).

Pt supported on NMC or NMC with extra framework magnesium catalysts (Pt/MgNMC-5%, Pt/Mg-NMC-10% and Pt/Mg-NMC-15%) were synthesized by the wetness impregnation reduction method assisted by ultrasonication. Typically, NMC or NMC with extra framework magnesium (0.1 g) was dispersed in deionized water (10 mL) in a beaker by ultrasonication, H_2PtCl_6 aqueous solution of the required concentration to obtain a content of 1 wt% Pt was added into the beaker, and the suspension was ultrasonicated for 10 mins, then NaBH_4 aqueous solution (0.1 mol/L) was injected quickly into the solution and kept under ultrasonication for another 10 mins. Subsequently, the beaker was placed on a stirrer for 2 h to equilibrate. The product was collected by filtration and washed with deionized water several times. The resulting black powder was dried in an oven overnight at 110 °C and collected for catalytic tests. For comparison, Pt/MgO-NMC-10% was also prepared following the above procedure.

2.2 Catalyst characterization

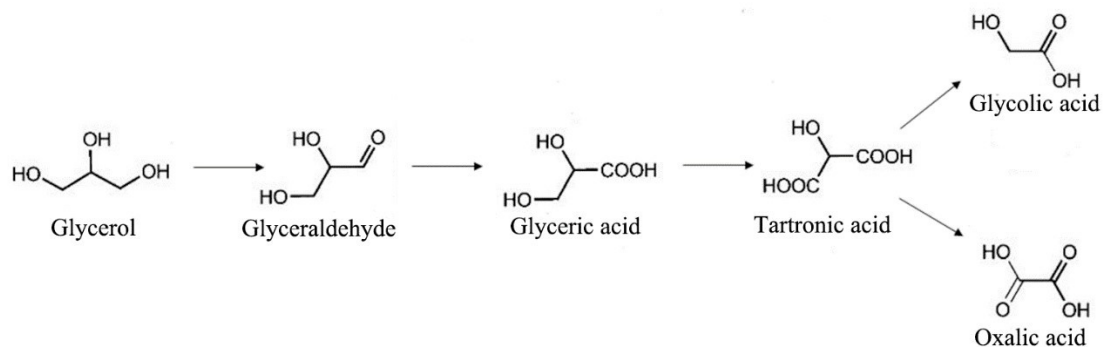
The contents of C, N, H and O in various carbon samples were determined using a PerkinElmer 2400 Series-II CHN/O Elemental Analyzer. ICP-OES analysis was conducted on Thermo Fisher iCAP 7600 series inductively coupled plasma optical emission spectrometry. The catalysts were digested in aqua regia ($\text{HCl}/\text{HNO}_3=3:1$) at 373 K for 6 h and then diluted with deionized water to a certain volume before analysis. TEM images of the samples were recorded by

using a FEI Tecnai G2 F20 S-Twin. Powder XRD patterns of the samples were obtained with a Bruker D8 Advance diffractometer with CuK α radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and 40 mA. XPS spectra were measured on a Thermo Scientific Escalab 250Xi by using an AlK α radiation source ($h\nu=1486.8 \text{ eV}$). The binding energy was calibrated by taking the C1s peak (BE=284.8 eV) as a reference. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gauss/Lorentz peak shape. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) to the integrated peak areas. Fourier transform infrared (FTIR) spectra were measured at room temperature with an FTIR spectrometer (Thermo Scientific, Nicolet-6700) using the KBr pellet technique. N₂ adsorption–desorption isotherms were obtained by using Micromeritics ASAP 2020 instrument at -196°C. Before the measurements, the samples were degassed under vacuum for approximately 12 h at 150 °C. CO₂ temperature-programmed desorption (TPD) was performed by using Micromeritics Autochem II 2920 Chemisorption Analyzer. The samples ($\approx 50 \text{ mg}$) were placed in a U-type quartz cell and pretreated in He flow at 900 °C for 1 h to remove the surface oxygen containing functional groups, and then the sample was cooled to 50 °C in flowing He. CO₂ was introduced and allowed to adsorb at 50 °C for 1 h. The sample was then purged with dry helium at the same temperature to remove weakly adsorbed CO₂. Finally, the sample was heated at a linear rate of 10 °C/min under dry helium to 800 °C.

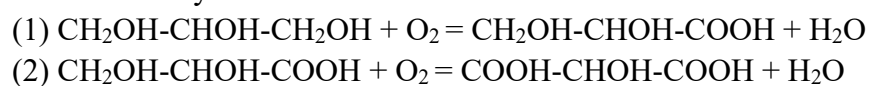
2.3 Catalytic activity measurement

Glycerol (GLY) oxidation was performed in a 50 mL three-necked flask equipped with a gas supply system, magnetic stirrer, condenser, and temperature controller. The reaction procedures were as follows: 25 mL of 0.3 mol/L GLY aqueous solution and a certain amount of catalyst (glycerol/Pt metal = 1000 mol/mol) were added into the reactor. O₂ (99.9%) was introduced into the reactor at 50 mL/min via a mass-flow controller at atmospheric pressure. After a certain reaction time at 60 °C, the catalysts were removed by filtration, and the liquid products were analyzed by using HPLC equipped with an Aminex HPX-87H column (Bio-Rad Laboratories) and refractive index (RI) detector. The analysis conditions were set as follows: eluent, 5 mM H₂SO₄; flow rate, 0.6 mL/min; column temperature, 50 °C. The retention time and calibration curves for the observed products were determined by injecting the standard samples at different concentration levels.

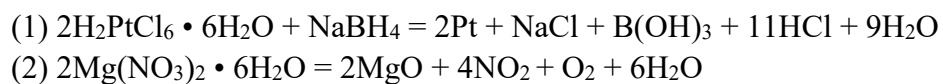
Scheme S1 Reaction pathway for the oxidation of GLY



The main catalytic reactions are:



The main stoichiometric equations for the catalyst preparation of catalysts are :



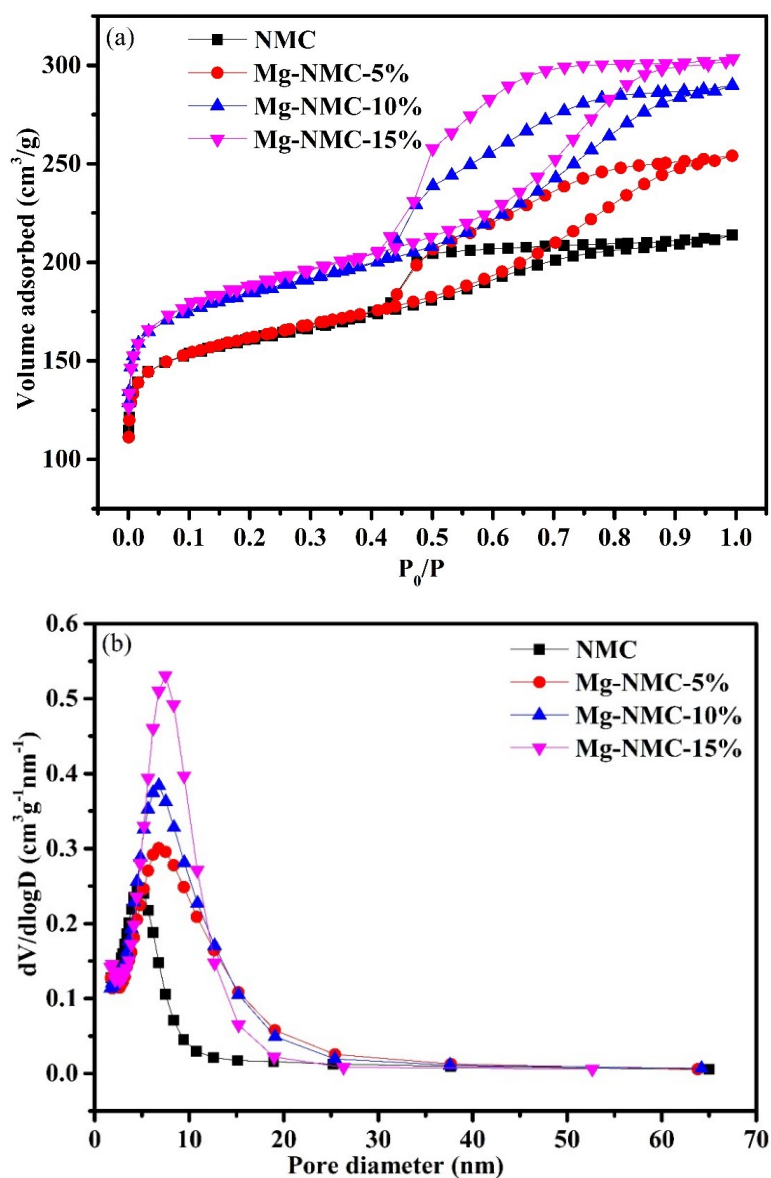


Figure S1 The nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution (b) of NMC, Mg-NMC-5%, Mg-NMC-10%, and Mg-NMC-15%.

Table S1 Textual properties of various carbon samples.

Samples	Carbon (m ² /g)	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{external} (m ² /g)	D _{BJH} (nm)
NMC	501.4	343.2	158.2	4.8	
Mg-NMC-5%	533.4	357.2	176.2	6.7	
Mg-NMC-10%	576.0	388.4	187.7	6.8	
Mg-NMC-15%		590.4	383.9	206.5	7.5

S_{BET} : BET surface area; S_{micro} : t -plot micropore area; S_{external} : t -plot external area; D_{BJH} : BJH pore size by adsorption branch.

Table S2 Chemical composition of various carbon samples measured by elemental analyzer and XPS.

CHN/O Elemental Analysis (mass%)													
Carbon Samples	C	Sample 1			Sample 2				Sample 3			M. V.	
		N	O	H	C	N	O	H	C	N	O	H	N
NMC	82.67	7.24	8.68	1.41	83.17	6.81	8.46	1.56	81.98	6.35	9.97	1.70	6.80
Mg-NMC-5%	79.72	7.03	9.96	1.53	79.12	7.22	10.03	1.75	78.51	6.94	11.24	1.59	7.06
Mg-NMC-10%	77.81	6.97	11.01	1.64	77.96	7.35	10.78	1.29	77.31	6.74	12.01	1.17	7.02
Mg-NMC-15%	76.41	7.27	11.59	1.83	76.72	7.16	12.08	1.36	75.74	7.38	12.56	1.48	7.27

XPS analysis (atom%)													
NMC	84.07	7.94	7.99	NA	84.73	7.52	7.75	NA					
Mg-NMC-5%	81.94	7.72	9.43	NA	81.94	7.86	9.35	NA	83.86	7.01	9.13	NA	7.49
Mg-NMC-10%	80.65	7.81	10.31	NA	80.57	8.09	10.13	NA	81.17	7.63	10.37	NA	7.74
Mg-NMC-15%	79.88	8.05	10.81	NA	79.31	7.96	11.45	NA	80.05	7.35	11.29	NA	7.75
									78.79	8.02	11.81	NA	8.01

M. V.: Mean Value

Table S3 Magnesium contents of various carbon samples measured by XPS and ICP.

Carbon Samples	XPS results (atom%)				ICP results (mass%)			
	Sample 1	Sample 2	Sample 3	M. V.	Sample 1	Sample 2	Sample 3	M. V.

Mg-NMC-5%	0.91	0.85	0.83	0.86	1.04	0.96	0.98	0.99
Mg-NMC-10%	1.23	1.21	1.31	1.25	1.51	1.43	1.56	1.50
Mg-NMC-15%	1.26	1.28	1.38	1.31	1.58	1.54	1.62	1.58

M. V.: Mean Value

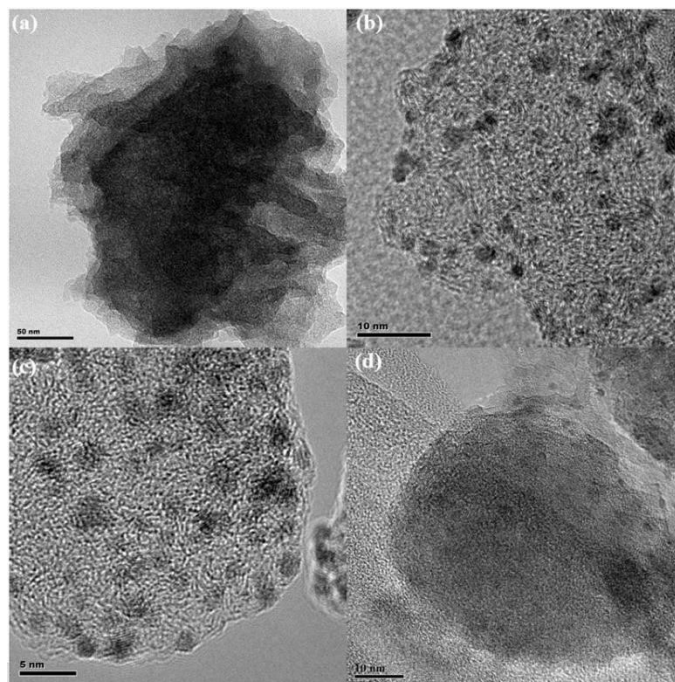


Figure S2 TEM images of NMC (a), Pt/NMC (b), Pt/Mg-NMC-10% (c), and Pt/MgO-NMC-10% (d).

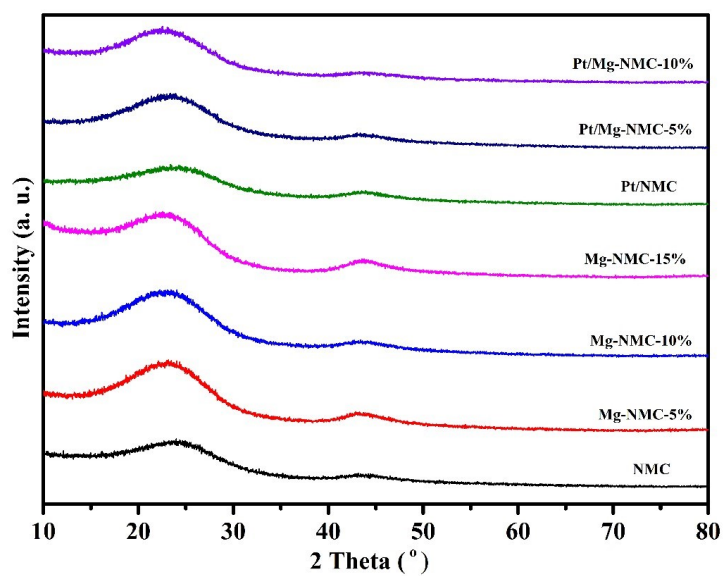


Figure S3 XRD patterns of NMC with extra framework magnesium and Pt/NMC with extra framework magnesium.

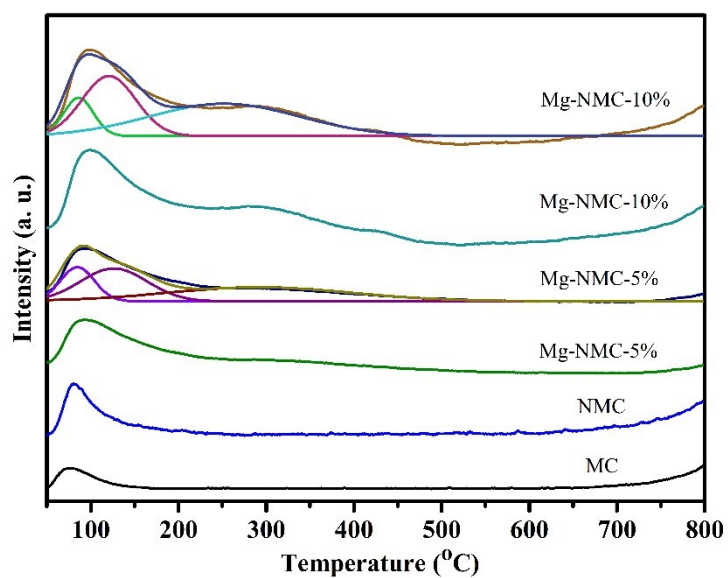


Figure S4 CO₂-TPD profile of MC and Peak fitting for CO₂-TPD profiles of Mg-NMC-5% and Mg-NMC-10%

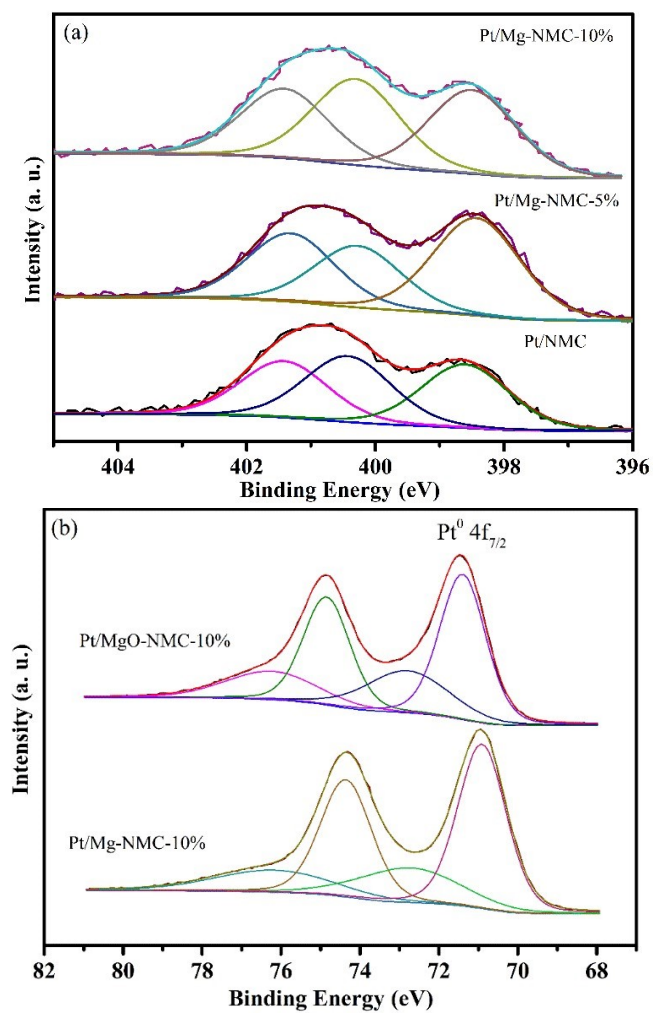


Figure S5 (a) XPS N 1s spectra of Pt/NMC, Pt/Mg-NMC-5% and Pt/Mg-NMC-10%.

(b) XPS Pt 4f spectra of Pt/Mg-NMC-10% and Pt/MgO-NMC-10%;

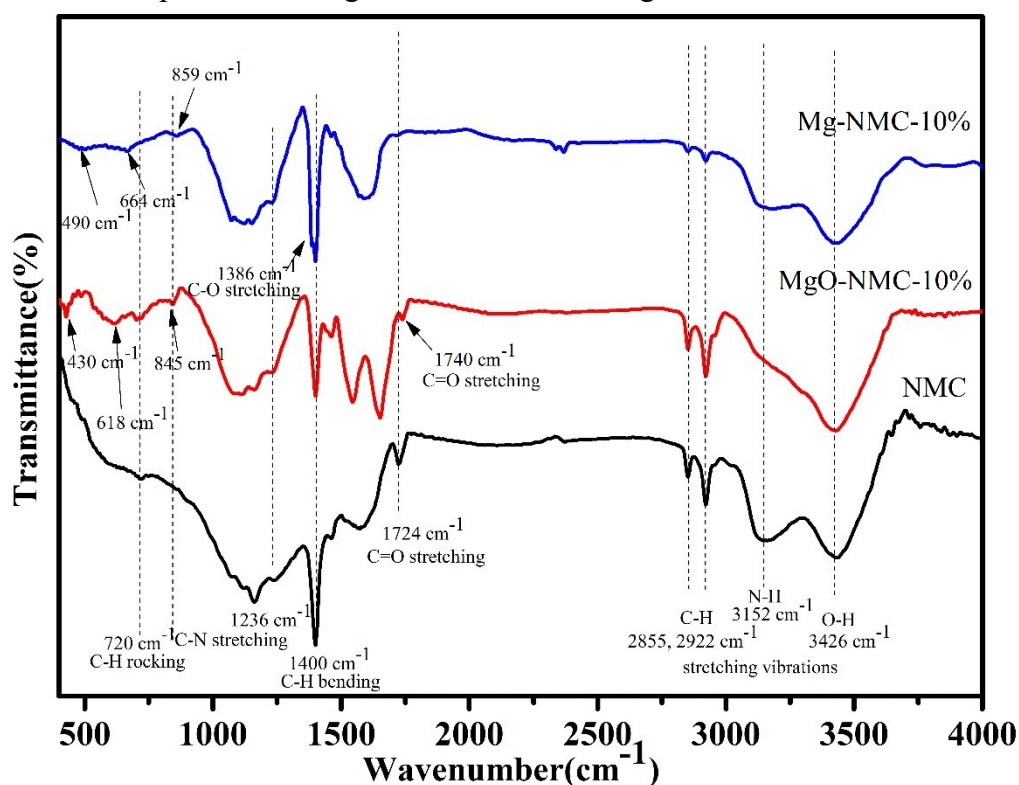


Figure S6 FT-IR spectra of NMC, MgO-NMC-10%, and Mg-NMC-10%.

Peak assignment:³⁻⁵ The peaks at 3426 and 3152 cm^{-1} are assigned to the stretching vibrations of O–H and N–H groups, respectively. The peaks at 2922 and 2855 cm^{-1} are attributed to the stretching vibrations of C–H groups. The sharp peaks at 1400 cm^{-1} can be assigned to the C–H bending vibration. The peak at 1236 cm^{-1} correspond to CN stretching vibration. The peak at 1386 cm^{-1} in Mg-NMC-10% can be assigned to the stretching vibration of C–O.

Table S4 Catalytic performance of various catalysts for GLY oxidation under basefree condition^a.

Catalysts	T (°C)	GLY Conv. (%)	Selectivity (%)			
			GLA	TA	OA	GA
Pt/NMC	60	78.5	76.3	7.7	2.2	3.7
Pt/Mg-NMC-5%	60	85.8	34.4	43.1	6.3	5.4
Pt/Mg-NMC-10%	60	87.2	14.2	60.2	7.5	6.2
Pt/Mg-NMC-15%	60	88.9	10.8	58.3	9.8	7.9

Pt/MgO-NMC 60 47.4 67.6 12.4 4.7 5.1

[a] Reaction conditions: 25 mL GLY solution (0.3 mol/L), GLY/Pt metal (mol/mol) = 1000, flow rate = 50 mL/min, reaction time = 6 h; GLA: Glyceric acid; TA: Tartronic acid; GA: Glycolic acid; OA: Oxalic acid;

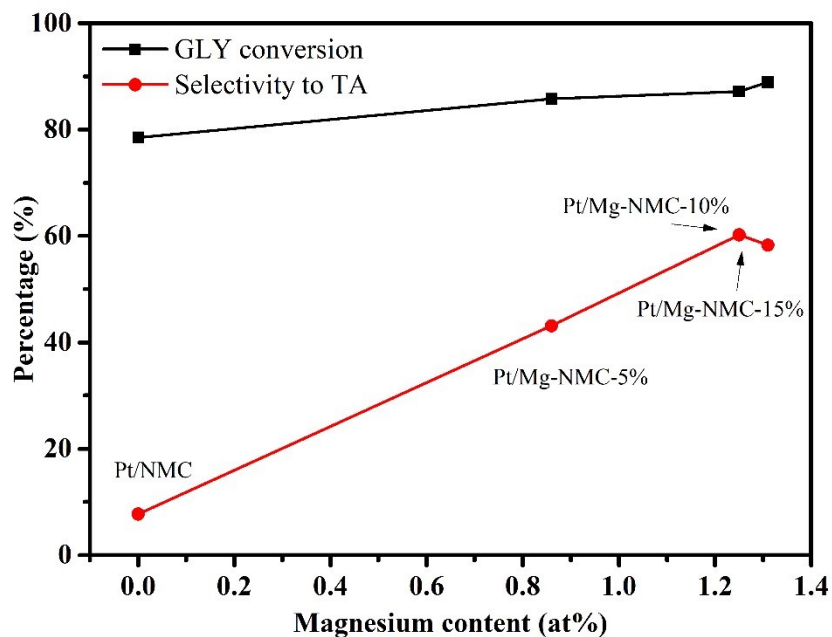


Figure S7 The relationship between the catalytic performance of Pt/NMC with extra framework magnesium catalysts and magnesium content (at%) measured by XPS in NMC with extra framework magnesium.

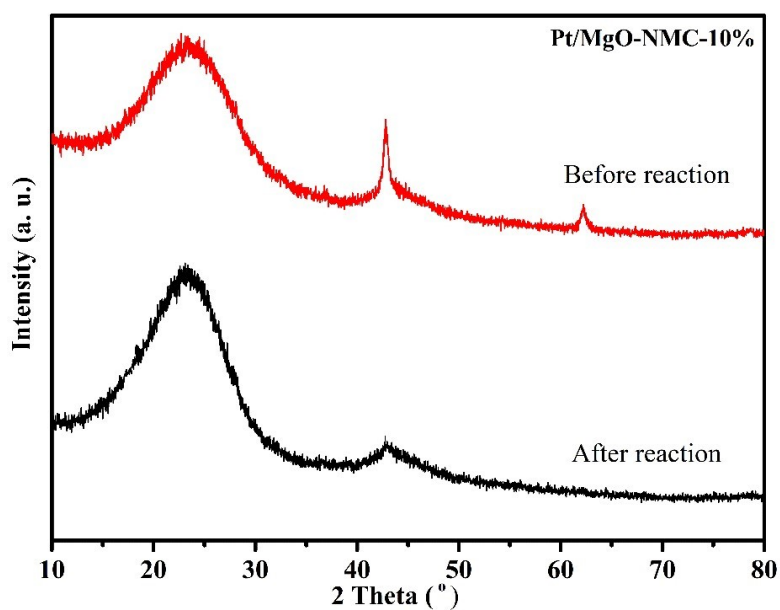


Figure S8 XRD patterns of Pt/MgO-NMC-10% before and after reaction.

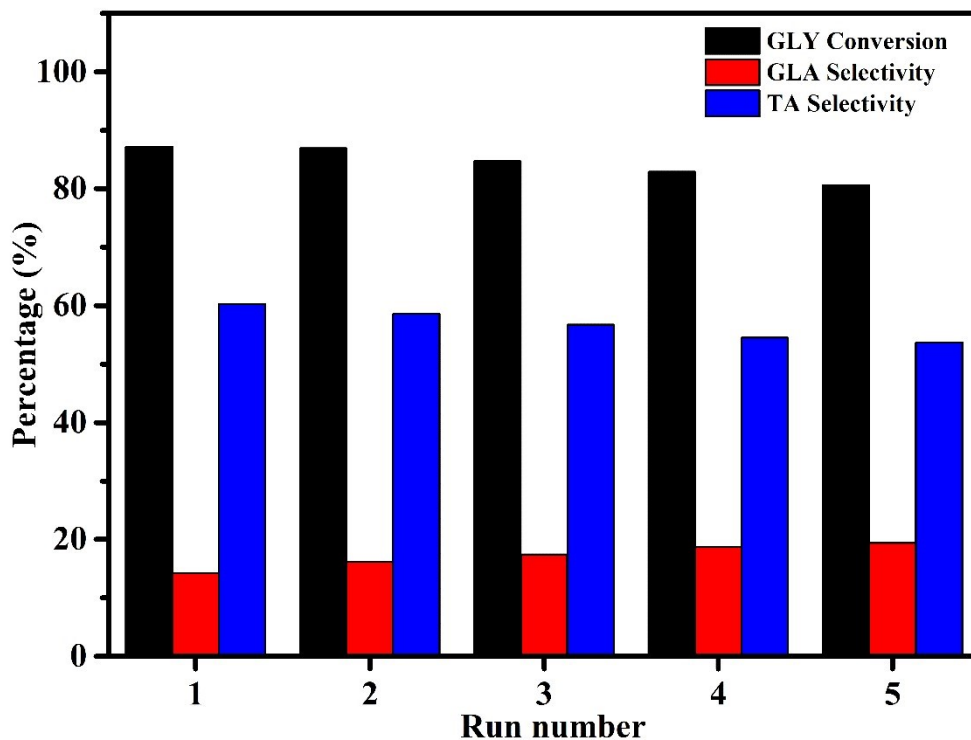


Figure S9 Reusability of Pt/Mg-NMC-10% in GLY oxidation under base free condition at 60 °C.

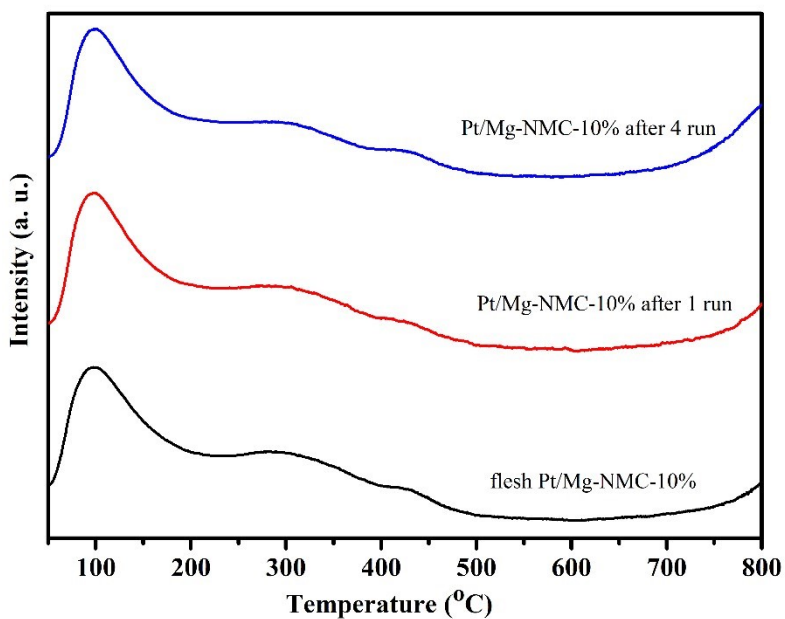


Figure S10 CO₂ TPD profiles of Mg-NMC-10%, Mg-NMC-10% after 1 run, and Mg-NMC-10% after 4 runs.

References

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