Oxidative Esterification of Renewable Furfural on Cobalt Dispersed on Ordered Porous Nitrogen-doped Carbon

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1. Molecular sieve preparation

1.1 Preparation of MCM-41

Pure silica MCM-41 was obtained by sol-gel synthesis according to the literature [1]. 1.6 g of hexadecyltrimethyl ammonium bromide (CTAB) was added to the solution containing 8.0 ml of NaOH solution (2 M) in deionized water (76 g) stirring at room temperature for 0.5h. Then, 7.6g tetraethyl orthosilicate (TEOS) was added dropwise. After stirring at room temperature for 0.5～1 h, transferred to a 100 ml Teflon-lined autoclave and submitted to a hydrothermal process at 373 K for another 3 days. The collected product was washed with deionized water and dried at 70 °C followed by calcination at 550 °C for 6 h with rate of 1 °C/min to remove the residual surfactants.

1.2 Preparation of SBA-15

SBA-15 was synthesized according to the literature [2]. 2 g triblock copolymer $EO_{20}PO_{70}EO_{20}$（P123）was dissolved in 15 g deionized water and 60 ml HCL solution (2M) and kept stirring until the solution became homogeneous. Then 4.25 g tetraethyl orthosilicate (TEOS) was added dropwise into the solution. After stirred for 24 h at 40 ℃， the solution was transferred to a 100ml Teflon-lined autoclave and submitted to a hydrothermal process at 373 K for another 3 days. The collected product was washed with deionized water and dried at 70 °C followed by calcination at 500 °C for 6 h with rate of 0.75 °C/min to remove the residual surfactants.

2. Supplementary Figures and Tables

Table S1 Particle size and cell diameter of MCM-41 and SBA-15.

Plane	MCM-41	SBA-15
	a (nm)	a (nm)
(100)	4.9	12.2
(110)	5.0	11.8
(200)	4.8	11.7

Particle size and cell diameter of MCM-41 and SBA-15 calculated from different planes according Bragg's law

Table S2. Hole structure data and elemental analysis of Co-NOPC catalysts.

Sample	Surface area[a](m^2/g)	Pore size[b](nm)	wall thickness[c](nm)
MCM-41	860	3.2	1.7
SBA-15	567	4.8	7.1
ZSM-5	274	6.1	-

[a] Surface area evaluated by using the BET model.

[b] Pore size evaluated by using the BJH model.

[c]Pore wall thickness is defined as the difference between the average unit cell parameter and the pore size.

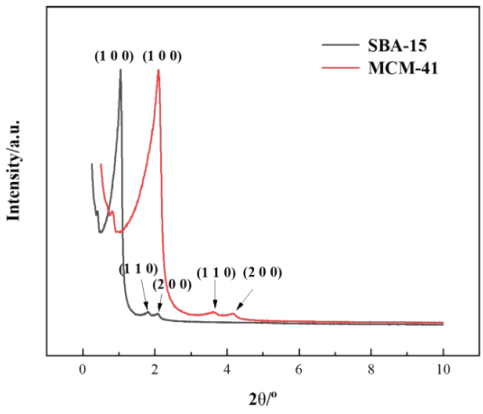

Fig. S1 Small angle XRD patterns of MCM-41 and SBA-15.

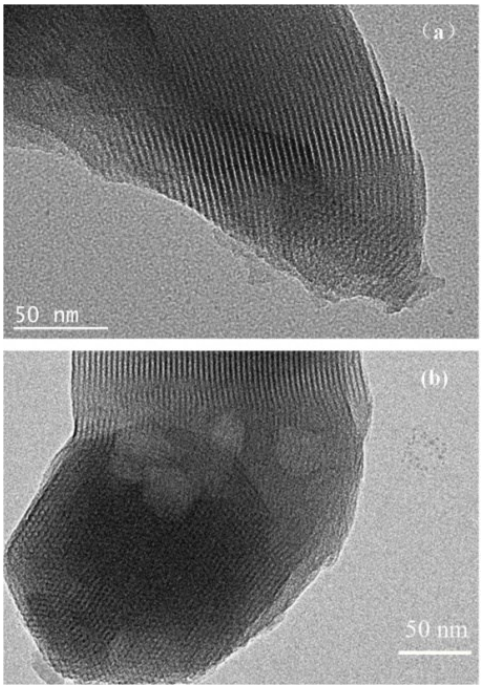

Fig. S2 TEM image of MCM-41(a) and SBA-15 (b).

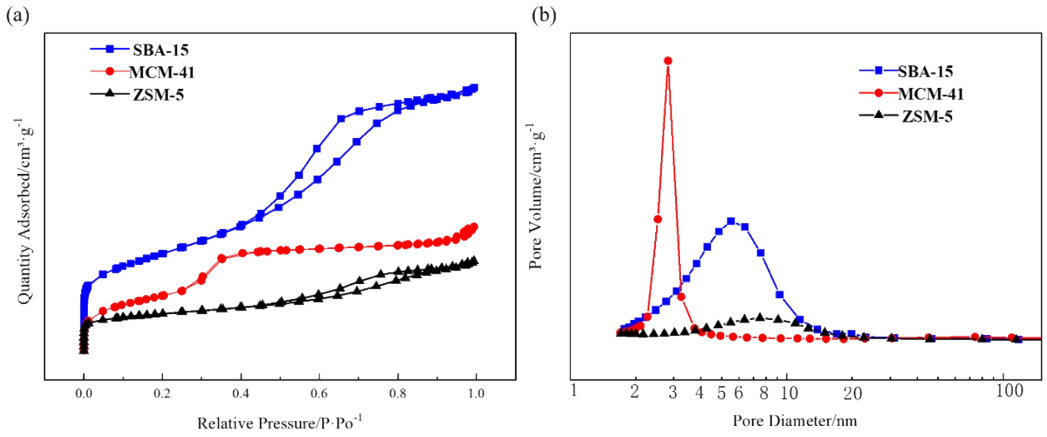

Fig. S3. (a) N_2 adsorption isotherm linear plot of molecular sieves, (b) pore size distribution of molecular sieves.

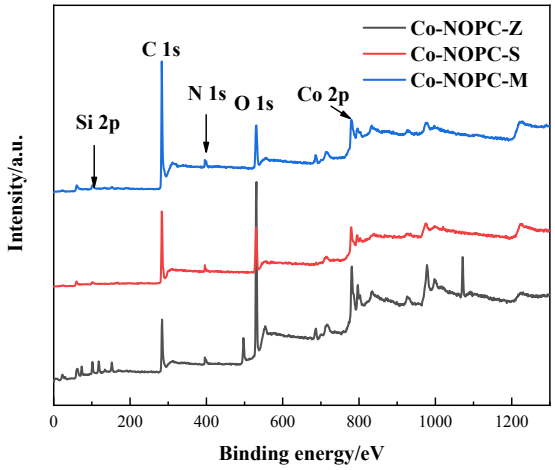

Fig. S4. XPS spectra of Co-NOPC Survey spectrum.

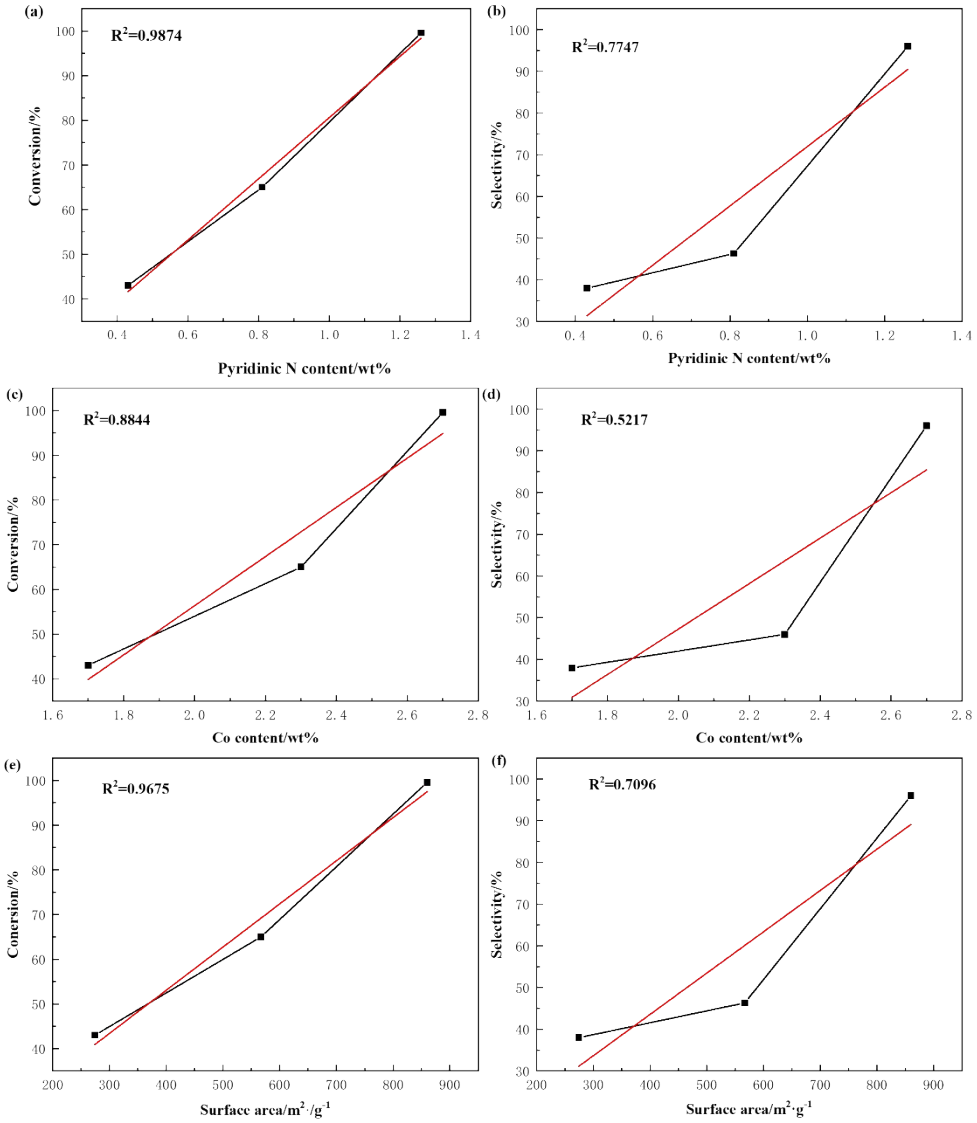

Figure.S5 Relationship between the content of pyridine nitrogen with conversion (a) and selectivity (b). Relationship between the content of Co with conversion (c) and selectivity (d). Relationship between surface area with conversion (e) and selectivity (f).

References

1. S. Molaei, T. Tamoradi, M. Ghadermazi.et.al, Synthesis and characterization of MCM-41@AMPD@Zn as a novel and recoverable mesostructured catalyst for oxidation of sulfur containing compounds and synthesis of 5-substituted tetrazoles, Microporous & Mesoporous Materials, (2018) S1387181118303585.
2. J. Du, H. Xu, J. Shen.et.al, Catalytic dehydrogenation and cracking of industrial dipentene over M/SBA-15 (M = Al, Zn) catalysts, Applied Catalysis A General, 296 (2005) 186-193.