Supplementary Information (SI) for Catalysis Science & Technology.

Electronic Supplementary Information

Heteroatom-assisted oxygen vacancies in cerium oxide catalysts for efficient synthesis of dimethyl carbonate from CO_2 and methanol

Niladri Maity,[a,*] Samiyah A. Al-Jendan,[a] Samir Barman,[a] Nagendra Kulal[a] and E. A. Jaseer [a]

[a]Interdisciplinary Research Center for Refining and Advanced Chemicals, King Fahd University for Petroleum & Minerals, Dhahran31261, Saudi Arabia. E-mail: niladri.maity@kfupm.edu.sa

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1. Elemental microanalysis of the synthesized $CeeO_2$ nanomaterials

Table S1: Elemental microanalysis of cerium nanomaterials

Compound	Temperature (°C)	Wt. (%)	
		N	S
CeO_2-NR	80	-	-
CeO_2-NR	600	-	-
S-CeO_2-NR	80	-	0.46
S-CeO_2-NR	600	-	0.18
N-CeO_2-NR	80	0.30	-
N-CeO_2-NR	600	0.20	-

2. Crystallite size calculation from PXRD.

Table S2: Crystallite size measured from PXRD for the CeO_2 nanomaterials.

Materials	Crystallite size (nm)			
	(111)[a]	(200)[b]	(220)[c]	(311)[d]
CeO_2-NR	10.4	9.63	10.4	9.2
S-CeO_2-NR	9.9	9.0	9.5	8.9
N-CeO_2-NR	10.1	9.9	10.6	10.0
CeO_2-NP	17.6	18.9	17.8	17.4

Estimated from [a](111) plane, [b](111), [c](111) and [d](111) of PXRD analysis.

3. Oxygen vacancy concentration data from RAMAN spectra

Table S3: Oxygen vacancy concentrations data

Compound	Oxygen vacancy concentration ($\times 10^{13}$ vacancies cm^{-3})
CeO_2-NP	1.51
CeO_2-NR	4.59
S-CeO_2-NR	5.56
N-CeO_2-NR	6.34

4. N_2 adsorption-desorption isotherm of CeO_2-NP

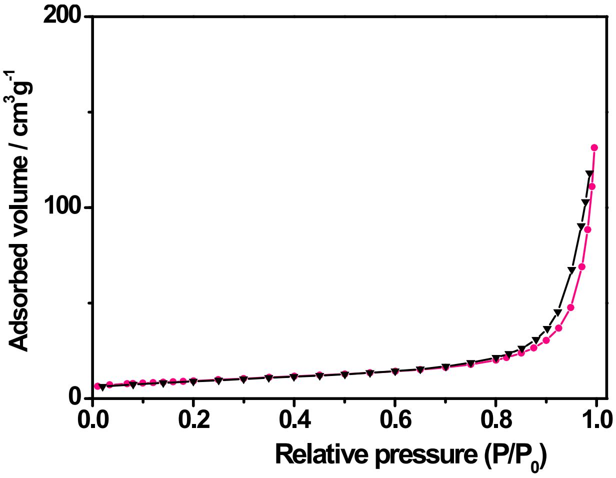


Fig. S1 N_2 adsorption-desorption isotherm of CeO_2-NP.

5. TEM image and lattice spacings of CeO_2-NP

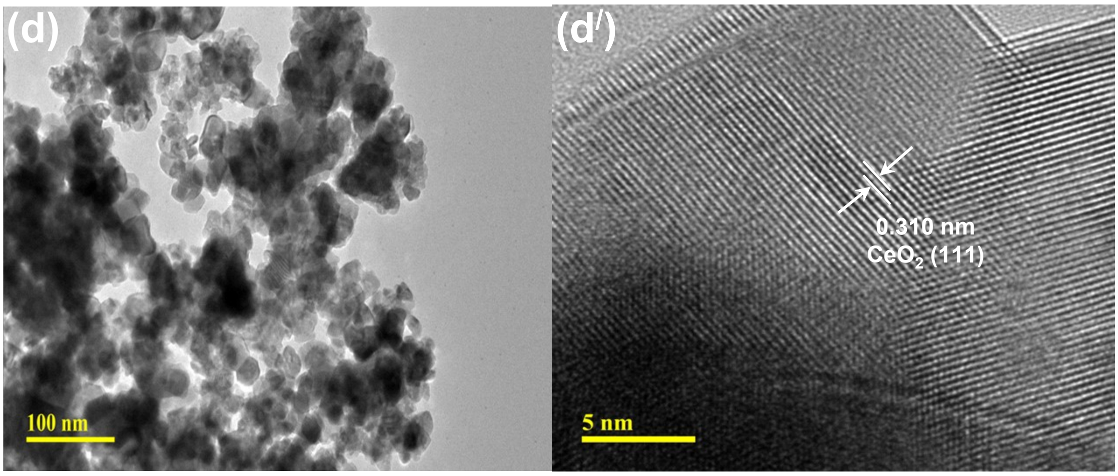


Fig. S2 (a) TEM image and (b) lattice spacings for CeO_2-NP.

6. CO_2-and NH_3-TPD plots for CeO_2-NP.

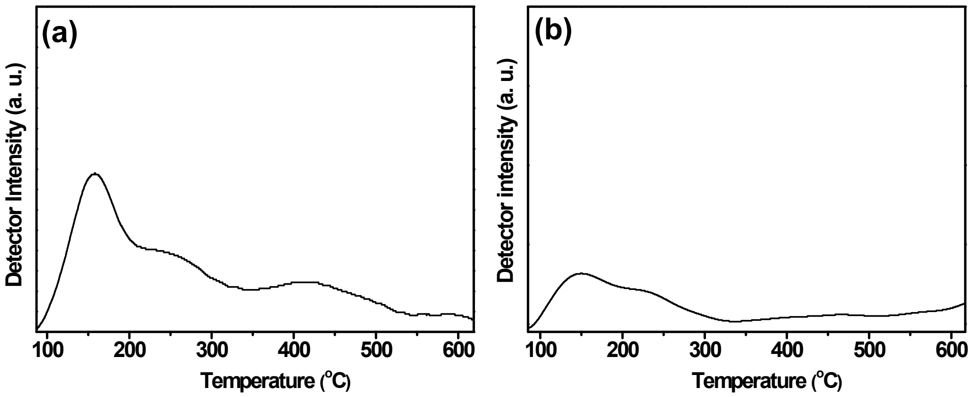


Fig. S3 (a) CO_2-TPD and (b) NH_3-TPD profiles of CeO_2-NP.

7. O1s binding energy spectra

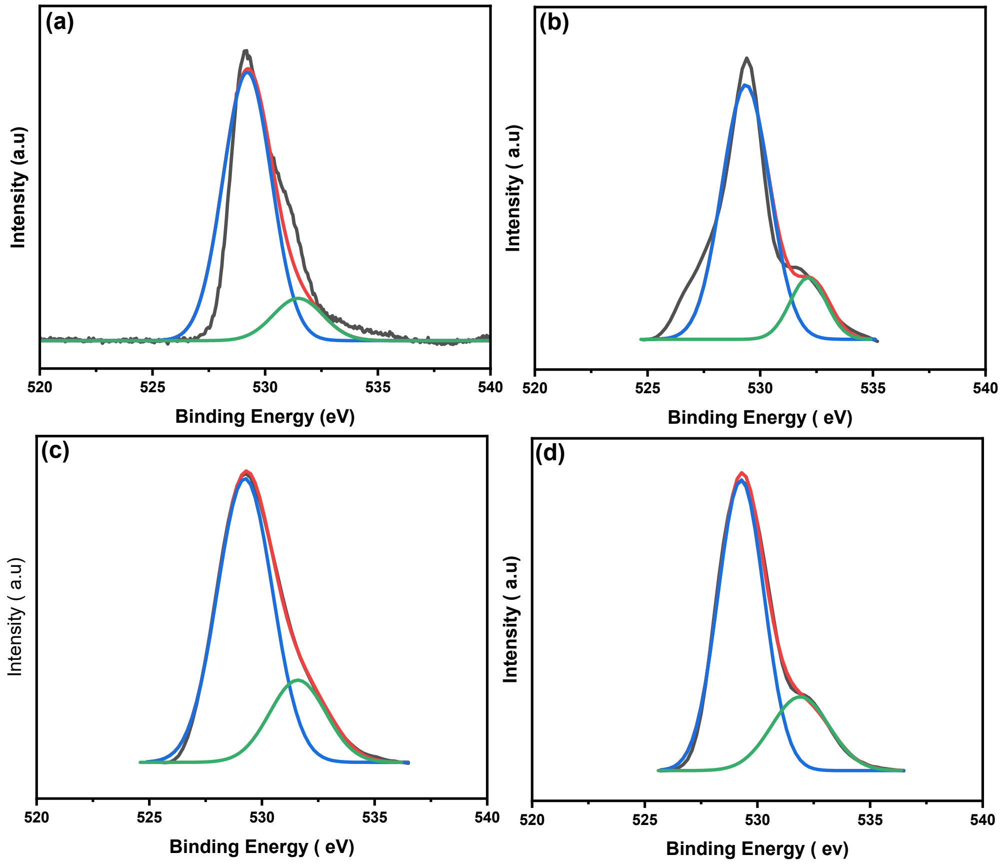


Fig. S4 O1s binding energy spectra of (a) CeO_2-NP, (b) CeO_2-NR, (c) S-CeO_2-NR and (d) N-CeO_2-NR.

8. Surface basicity and acidity data of the CeO_2 nanomaterials from CO_2- and NH_3-TPD

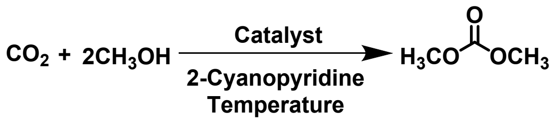
Table S4: The basicity and acidity of the CeO_2 nanomaterials.

Materials	Surface basicity[a] (Adsorbed CO_2) (mmol/g)	Surface acidity[b] (Adsorbed NH_3) (mmol/g)
CeO_2-NR	0.109	0.290
S-CeO_2-NR	0.113	0.298
N-CeO_2-NR	0.130	0.324
CeO_2-NP	0.099	0.048

[a]Estimated from CO_2-TPD. [b] Estimated from NH_3-TPD.

9. Performances of CeO_2-NP, CeO_2-NR, S-CeO_2-NR, N-CeO_2-NR towards the catalytic synthesis of DMC

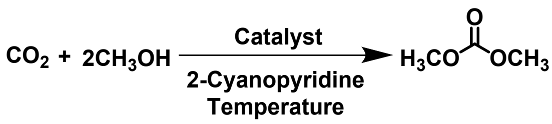
Table S5. Effect of calcination temperature on the performances of X-CeO_2-NR catalysts.



Entry	Catalysts	Calcination temp. (°C)	Dehydrating reagent	MeOH conversion (%)	DMC yield (mmol g_{cat}^{-1})	Selectivity (%)		
						DMC	Methyl picolinate	Methyl carbamate
1	N-CeO_2-NR	300	2-CP	1.2	5.7	100	0	0
2	N-CeO_2-NR	500	2-CP	4.1	20.3	100	0	0
3	N-CeO_2-NR	600	2-CP	22.7	113.3	100	0	0
4	N-CeO_2-NR	700	2-CP	22.0	110.0	100	0	0
5	N-CeO_2-NR	800	2-CP	14.3	70.7	100	0	0
6	S-CeO_2-NR	300	2-CP	1.1	5.3	100	0	0
7	S-CeO_2-NR	600	2-CP	9.9	49.7	100	0	0

Reaction conditions: 100 mg catalyst, Methanol (3.20 g, 100 mmol), 2-cyanopyridine (2-CP: 5.20 g, 50 mmol), CO_2 (4 MPa), 100 °C, 2 h.The DMC yield and selectivity were estimated using ^{1}H NMR spectra.

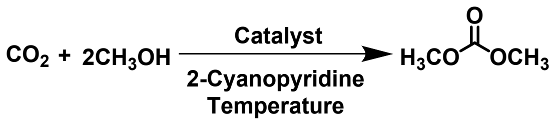
Table S6. Effect of CO_2 pressure and 2-CP on the performances of N-CeO_2-NR catalyst towards DMC yield.



Entry	CO_2 pressure (MPa)	Dehydrating reagent	MeOH conversion (%)	DMC yield (mmol g_{cat}^{-1})	Selectivity (%)		
					DMC	Methyl picolinate	Methyl carbamate
1[a]	4	2-CP	22.7	113.3	100	0	0
2[a]	0.4	2-CP	11.0	55.2	100	0	0
3[a]	0.1	2-CP	0.2	0.8	100	0	0
4[b]	4	2-CP	14.9	74.5	100	0	0
5	4	-	1.0	4.7	100	0	0

Reaction conditions: 100 mg catalyst, Methanol (3.20 g, 100 mmol), CO_2 (4 MPa), 100°C), 2 h.The DMC yield and selectivity were estimated using ^1H NMR spectra. [a]2-cyanopyridine (2-CP: 5.20 g, 50 mmol), [b]2-cyanopyridine (2-CP: 10.4 g, 100 mmol).

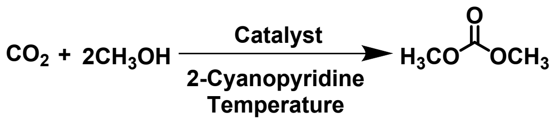
Table S7. Effect of reaction temperature on the performances of N-CeO_2-NR catalyst.



Entry	Reaction temp. (°C)	Dehydrating reagent	MeOH conversion (%)	DMC yield (mmol g_{cat}^{-1})	Selectivity (%)		
					DMC	Methyl picolinate	Methyl carbamate
1	100	2-CP	22.7	113.3	100	0	0
2	120	2-CP	39.6	196.7	99.2	0.5	0.3
3	140	2-CP	51.4	242.7	94.4	3.0	2.6
4	160	2-CP	47.9	190.0	75.2	14.4	10.4

Reaction conditions: 100 mg catalyst, Methanol (3.20 g, 100 mmol), 2-cyanopyridine (2-CP: 5.20 g, 50 mmol), CO_2 (4 MPa), 2 h.The DMC yield and selectivity were estimated using ^1H NMR spectra.

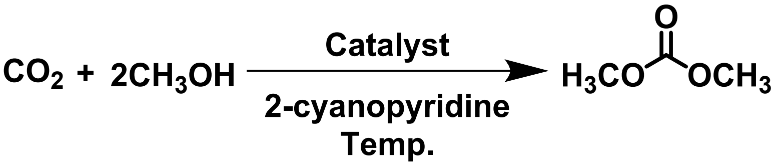
Table S8. Effect of reaction time on the performances of N-CeO_2-NR catalyst.



Entry	Reaction time (h)	Dehydrating reagent	MeOH conversion (%)	DMC yield (mmol g_{cat}^{-1})	Selectivity (%)		
					DMC	Methyl picolinate	Methyl carbamate
1	2	2-CP	22.7	113.3	100	0	0
2	12	2-CP	42.4	207.7	97.9	0.7	1.4
3	24	2-CP	33.6	80.7	64.9	33.4	1.7

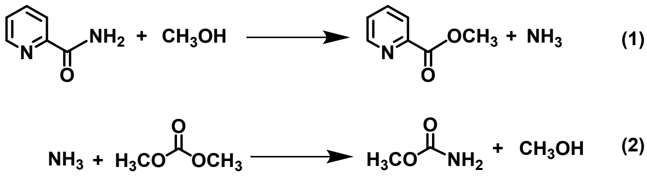
Reaction conditions: 100 mg catalyst, Methanol (3.20 g, 100 mmol), 2-cyanopyridine (2-CP: 5.20 g, 50 mmol), CO_2 (4 MPa), 100 °C. The DMC yield and selectivity were estimated using ^1H NMR spectra.

Table S9. Comparative catalytic efficiency of CeO_2 nanomaterials towards the yield of dimethyl carbonate from CO_2 and methanol.



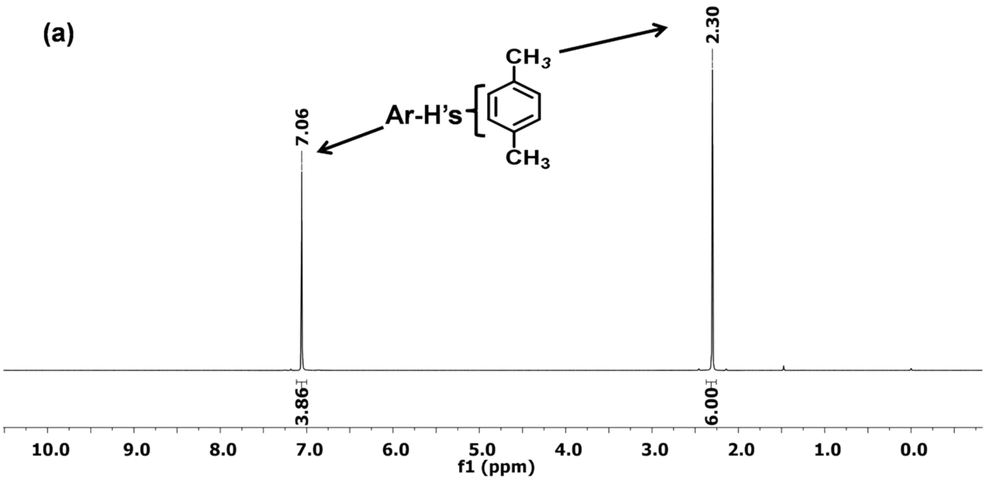
Entry	Catalysts	Catalyst wt. (mg)	Methanol (mmol)	2-CP (mmol)	CO_2 (MPa)	Temp. (°C)	Time (h)	MeOH conv. (%)	DMC Yield (mmol g_{cat}^{-1})	DMC Selectivity (%)
1	CeO_2-NP	100	100	50	4	100	2	0.2	0.8	100
2	CeO_2-NR	100	100	50	4	100	2	5.8	28.8	100
3	S-CeO_2-NR	100	100	50	4	100	2	9.9	49.7	100
4	N-CeO_2-NR	100	100	50	4	100	2	22.7	113.3	100

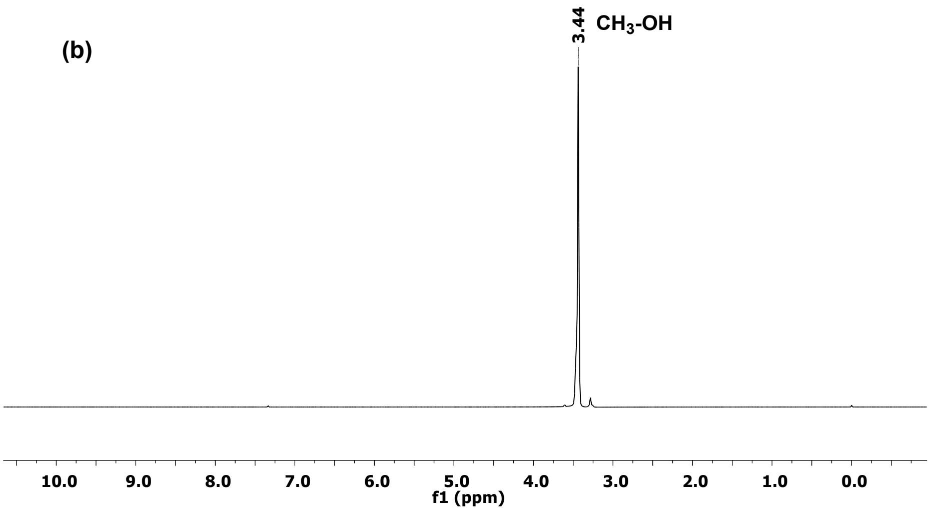
10. Formation of side products methyl picolinate and methyl carbamate during the synthesis of DMC

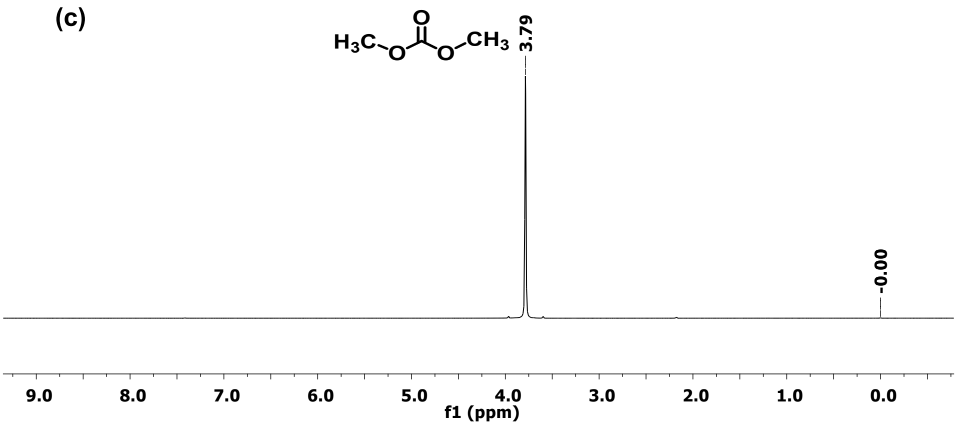


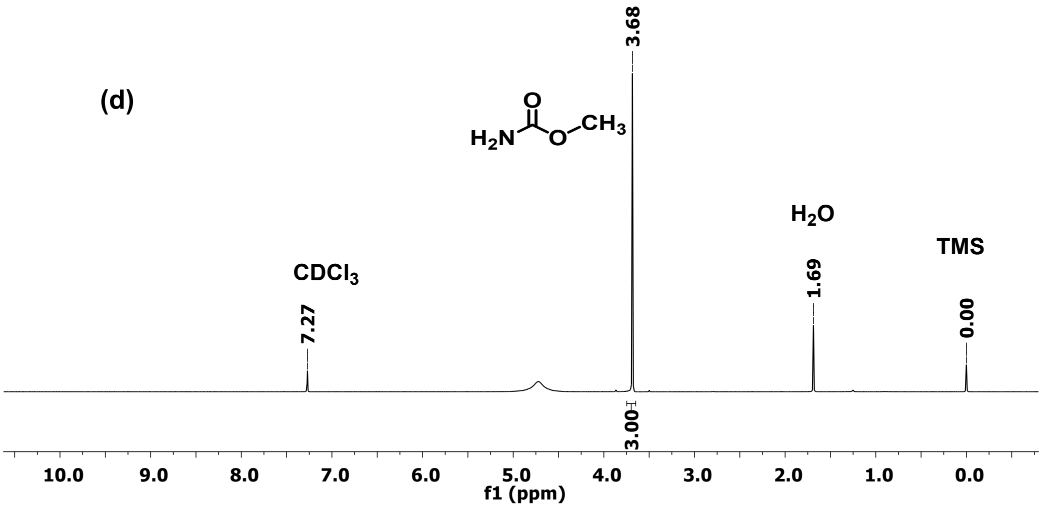
Scheme S1. The proposed routes towards the formation of side products methyl picolinate and methyl carbamate during the synthesis of DMC from CO_2 and methanol in the presence of 2-cyano pyridine.

11. Representative [1]H NMR spectra of standard compounds and the reaction mixture








(d)
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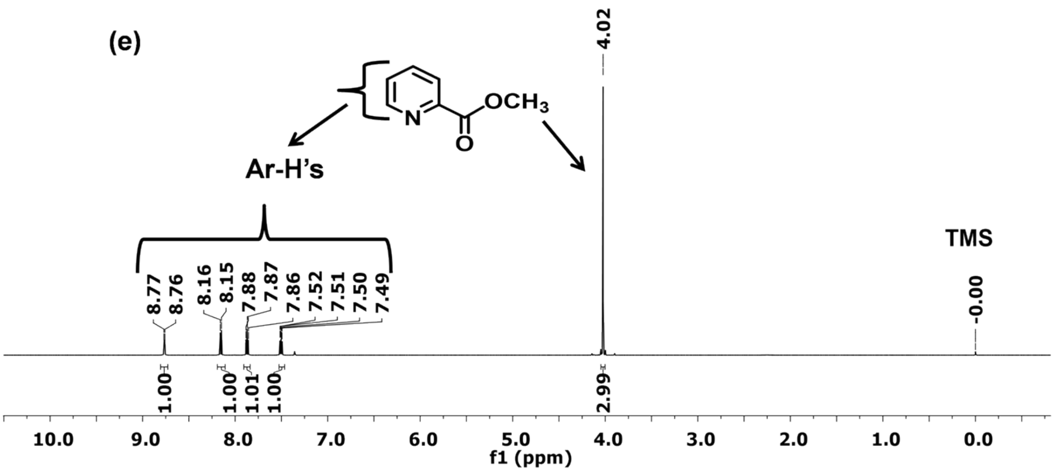
O
O
CH_3
H_2O
TMS
$CDCl_3$
7.27
1.69
0.00
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


(e)
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N
OCH_3
O
Ar-H's
TMS
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-0.00
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2.99
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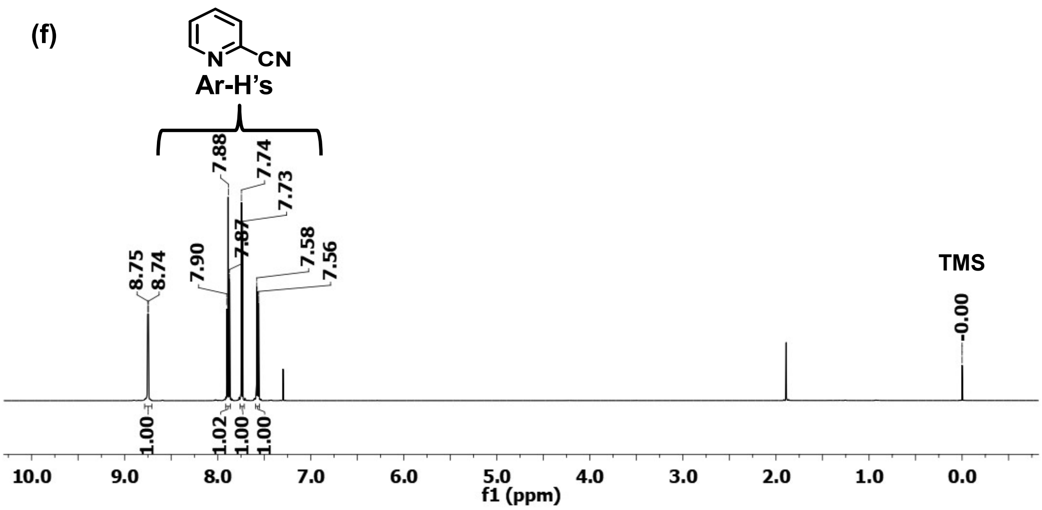
f1 (ppm)


(f)
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CN
Ar-H's
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TMS
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f1 (ppm)

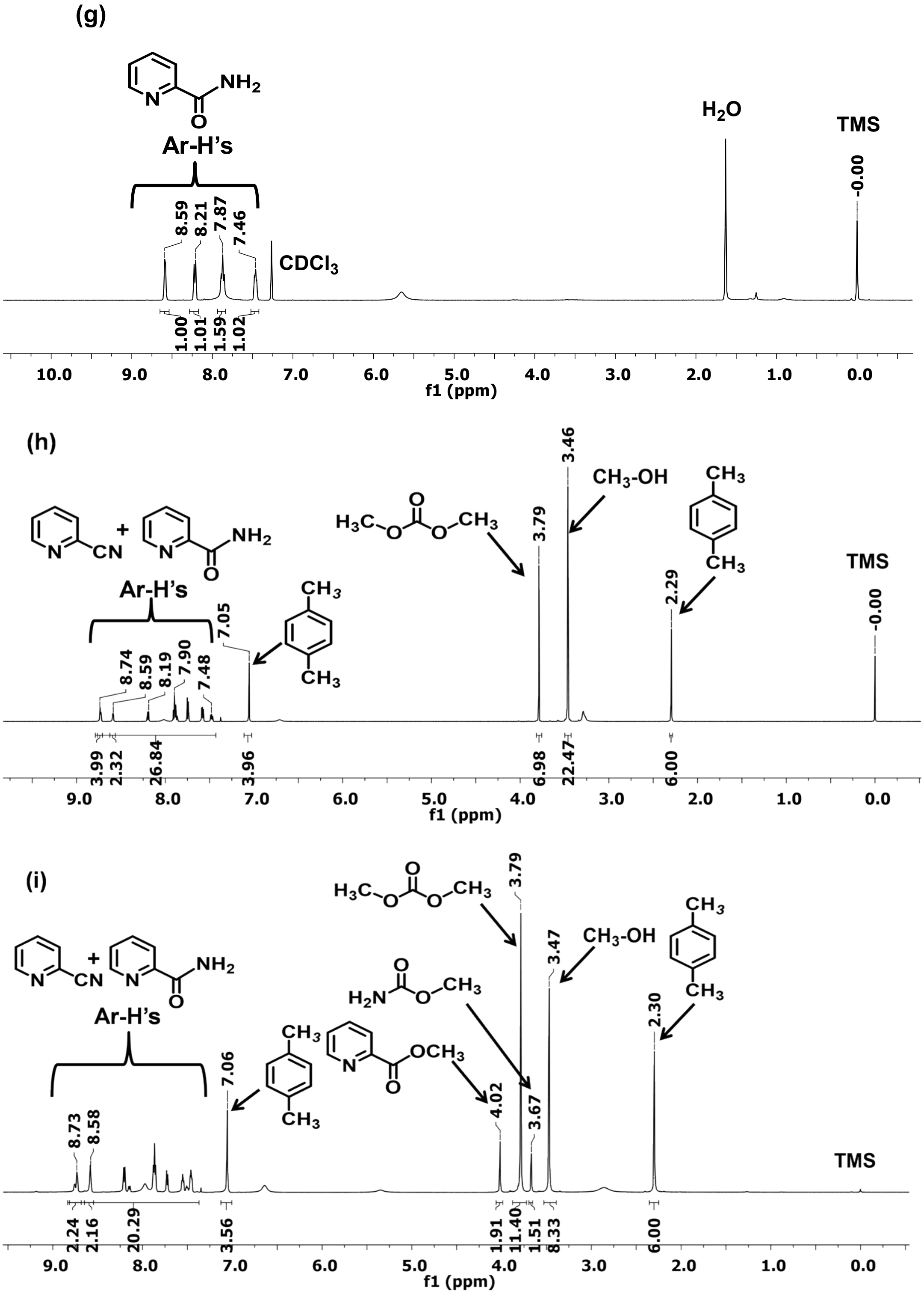


Fig. S5 [1]H NMR spectra of (a) *p*-Xylene, (b) methanol, (c) dimethyl carbonate, (d) methyl carbamate, (e) methyl picolinate, (f) 2-cyano pyridine, (g) piconilamide, (h) N-CeO_2-NR catalyzed reaction (Table S6, Entry 1) after 2 h at 100 °C, and (i) N-CeO_2-NR catalyzed reaction (Table S6, Entry 4) after 2 h at 160 °C.

12. The plot of surface acidity and basicity vs catalytic efficiency

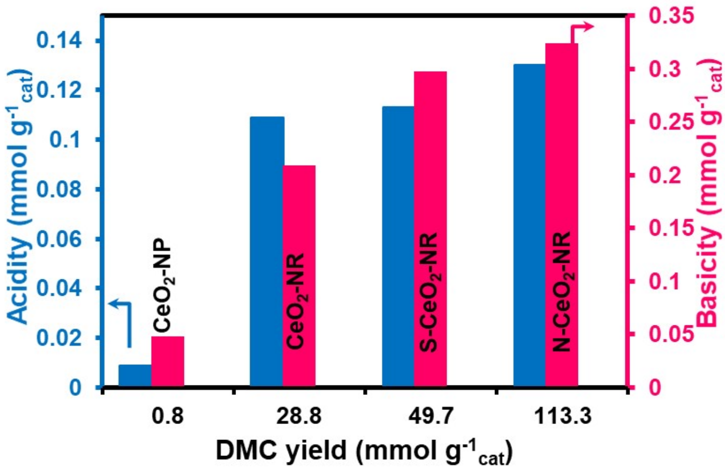
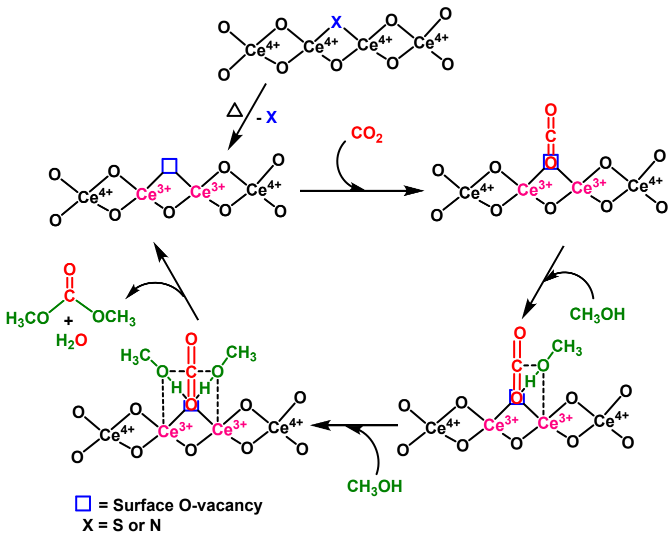


Fig. S6 Correlation between surface acity, surface basicity and catalytic efficiency (DMC yield) of the CeO_2 based nanocatalysts.

13. Proposed reaction mechanism



Scheme S2. Proposed reaction mechanism involving X-CeO_2-NR catalysts towards the synthesis of DMC from CO_2 and methanol.