Supplementary Material

Influence of Different Microstructures of Cobalt on the Catalytic Activity for Amination of Ethylene Glycol: Comparison of HCP Cobalt and FCC Cobalt

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Table S1 Catalytic performance of Co and Ni for amination of EG

Catalyst	Temp （℃）	X_{EG} （%）	Yield（Selectivity）（%）			
			MEA	EDA	PIP	MEA+EDA
hcp-Co (50-100 nm)	185	24.8	7.7 (31.1)	2.5 (10.1)	1.0 (3.9)	10.2 (41.2)
hcp-Co (100-300 nm)	185	25.2	8.2 (32.5)	2.5 (9.7)	1.0 (4.0)	10.7 (42.2)
fcc-Ni (100-200 nm)	185	13.7	1.8 (13.0)	0.1 (0.5)	0.2 (1.6)	1.9 (13.5)

Hcp-Co (50-100 nm): this work. Metal fcc-Ni and hcp-Co catalysts (100-300 nm) were prepared by co-precipitation method [1].

Reaction conditions: Initial hydrogen pressure =3 MPa, t=12 h, $m_{(EG)}$=1.12 g, $m_{(NH3)}$=10 g, a weight percentage of catalyst=10%.

X: conversion; EG: ethylene glycol; MEA: monoethanolamine; EDA: ethylenediamine; PIP: piperazine;

Table S2 Characterization of fcc-Co and hcp-Co catalyst.

Catalyst	H_2 adsorbed ($\mu mol\ g^{-1}$)	Co Dispersion (%)	BET surface area ($m^2\ g^{-1}$)	D[a] ($\mu mol\ g^{-1}$)
fcc-Co	85.6	0.34	4.56	57.1
hcp-Co	84.3	0.33	4.09	56.2

[a] *D* represents the concentration of surface active sites derived from H_2 and O_2 titration.

Table S3 The selectivity of products for catalytic amination of EG.

Catalyst	Temp (℃)	X_{EG} （%）	Selectivity（%）							
			MEA	EDA	PIP	AEP	HEP	DETA	HEEDA	Other degradation products
fcc-Co	175	24.8	33.5	14.0	6.7	1.7	1.6	0.6	2.7	39.2
	185	33.9	28.2	15.3	13.2	1.4	1.4	2.3	1.6	36.6
	195	35.4	24.5	14.5	16.2	1.3	1.2	1.6	1.6	39.1
hcp-Co	175	10.6	33.7	0.4	1.5	4.5	6.0	1.9	6.0	46.0
	185	24.8	31.1	10.1	3.9	1.7	2.6	0.8	3.2	46.6
	195	35.0	26.6	9.0	9.9	1.7	2.0	0.9	1.4	48.5

X: conversion; EG: ethylene glycol; MEA: monoethanolamine; EDA: ethylenediamine; PIP: piperazine; AEP: aminoethylpiperazine; HEP: hydroxyethylpiperazine; DETA: diethylenetriamine; HEEDA: hydroxyethylethylenediamine; Other degradation products：carbon monoxide, methanol, methylamine, methane, formaldehyde.

Table S4 Entropic contribution of EG dehydrogenation process (T=458 K).

Intermediate or transition state	TS (eV)			
	Co (111)	Co (0001)	Co (10-10)	Co (10-11)
$OHCH_2CH_2OH$	0.24378	0.24771	0.17619	0.14631
TS1	0.19826	0.30146	0.20310	0.21594
$OHCH_2CH_2O$	0.20837	0.21173	0.25479	0.20344
TS3	0.43394	0.44093	0.30483	0.20911
$OHCH_2CHO$	0.10520	0.10690	0.12330	0.13516

Table S5 Effect of initial hydrogen pressure on the amination of ethylene glycol.

Entry	Catalyst	Initial hydrogen pressure /MPa	X_{EG} （%）	Yield（Selectivity）（%）			
				MEA	EDA	PIP	MEA+EDA
1	hcp-Co	1	18.8	6.3 (33.4)	2.3 (12.2)	0.8 (4.2)	8.6 (45.6)
2	hcp-Co	2	22.7	7.3 (31.9)	2.5 (11.0)	0.8 (3.6)	9.8 (42.9)
3	hcp-Co	3	25.2	8.2 (32.5)	2.5 (9.7)	1.0 (4.0)	10.7 (42.2)
4	hcp-Co	4	24.9	8.1 (32.6)	2.3 (9.5)	0.9 (3.7)	10.4 (42.1)

Reaction conditions: T=185 ℃, t=12 h, $m_{(EG)}$=1.12 g, $m_{(NH3)}$=10 g, $m_{(H2O)}$=6 g ，a weight percentage of catalyst=10%.

X: conversion; EG: ethylene glycol; MEA: monoethanolamine; EDA: ethylenediamine; PIP: piperazine;

Table S6 Effect of reaction time on EG amination at different temperature.

Catalyst	Temp （℃）	Time （h）	X_{EG} （%）	Yield（Selectivity）（%）			
				MEA	EDA	PIP	MEA+EDA
fcc-Co	175	4	9.7	4.1 (41.8)	0.1 (0.5)	0.3 (2.7)	4.2 (42.3)
	175	8	18.6	8.7 (46.8)	2.3 (12.1)	2.3 (12.2)	11.0 (58.9)
	175	12	24.8	8.3 (33.5)	3.5 (14.0)	1.7 (6.7)	11.8 (47.5)
	185	4	13.2	7.8 (58.9)	0.7 (5.3)	0.7 (5.1)	8.5 (64.2)
	185	8	25.6	10.1 (39.3)	3.1 (11.9)	1.3 (5.0)	13.2 (51.2)
	185	12	33.9	9.6 (28.2)	5.2 (15.3)	4.5 (13.2)	14.8 (43.5)
	195	4	27.1	7.2 (26.6)	2.9 (10.5)	2.7 (10.0)	10.1 (37.1)
	195	8	29.7	10.1 (34.0)	3.3 (11.0)	3.2 (10.8)	13.4 (45.0)
	195	12	35.4	8.7 (24.5)	5.1 (14.5)	5.7 (16.2)	13.8 (39.0)
hcp-Co	175	4	6.6	2.7 (40.3)	0.1 (0.6)	0.2 (2.9)	2.8 (40.9)
	175	8	9.3	3.4 (36.4)	0.1 (0.5)	0.1 (1.4)	3.5 (36.9)
	175	12	10.6	3.6 (33.7)	<0.1(0.4)	0.2 (1.5)	3.6 (34.1)
	185	4	7.5	3.3 (44.1)	0.1 (1.1)	1.5 (19.9)	3.4 (45.2)
	185	8	17.8	8.2 (46.0)	1.2 (6.8)	1.1 (6.4)	9.4 (52.8)
	185	12	24.8	7.7 (31.1)	2.5 (10.1)	1.0 (3.9)	10.2 (41.2)
	195	4	18.7	5.8 (30.7)	0.7 (3.8)	0.5 (2.8)	6.5 (34.5)
	195	8	26.6	8.3 (31.0)	2.2 (8.1)	1.1 (4.2)	10.5 (39.1)
	195	12	35.0	9.3 (26.6)	3.2 (9.0)	3.5 (9.9)	12.5 (35.6)

Reaction conditions: Initial hydrogen pressure=3 MPa, $m_{(EG)}$=1.12 g, $m_{(NH3)}$=10 g, $m_{(H2O)}$=6 g, a weight percentage of catalyst=10%.

X: conversion; EG: ethylene glycol; MEA: monoethanolamine; EDA: ethylenediamine; PIP: piperazine.

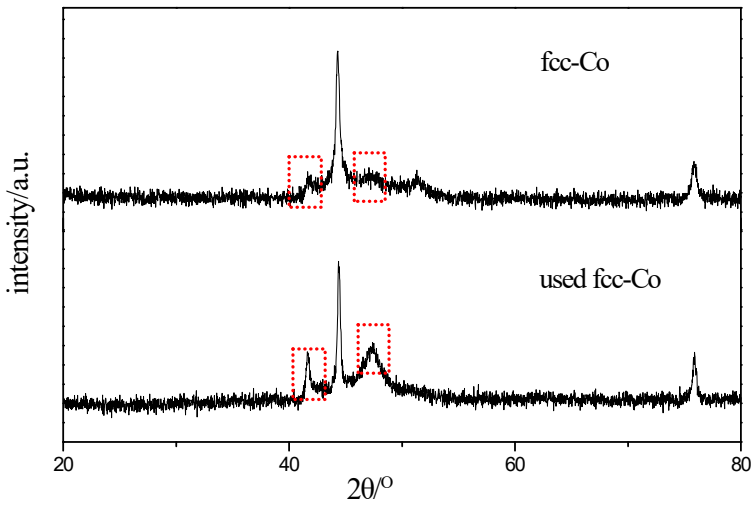
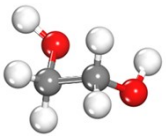
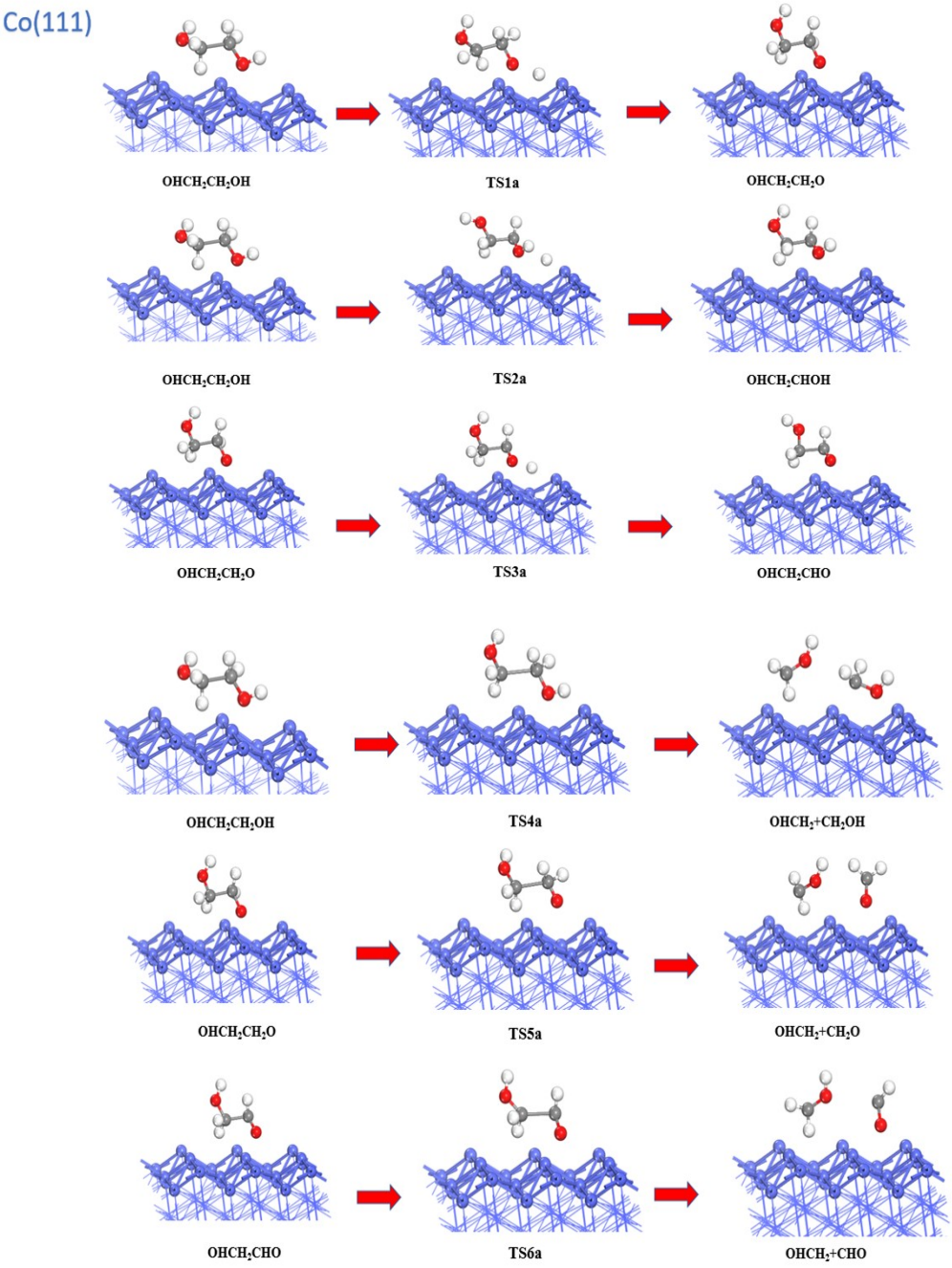


Fig.S1 XRD patterns of fcc-Co and used fcc-Co catalysts.



EG

Co


Co(111)
OHCH2CH2OH
TS1a
OHCH2CH2O
OHCH2CH2OH
TS2a
OHCH2CHOH
OHCH2CH2O
TS3a
OHCH2CHO
OHCH2CH2OH
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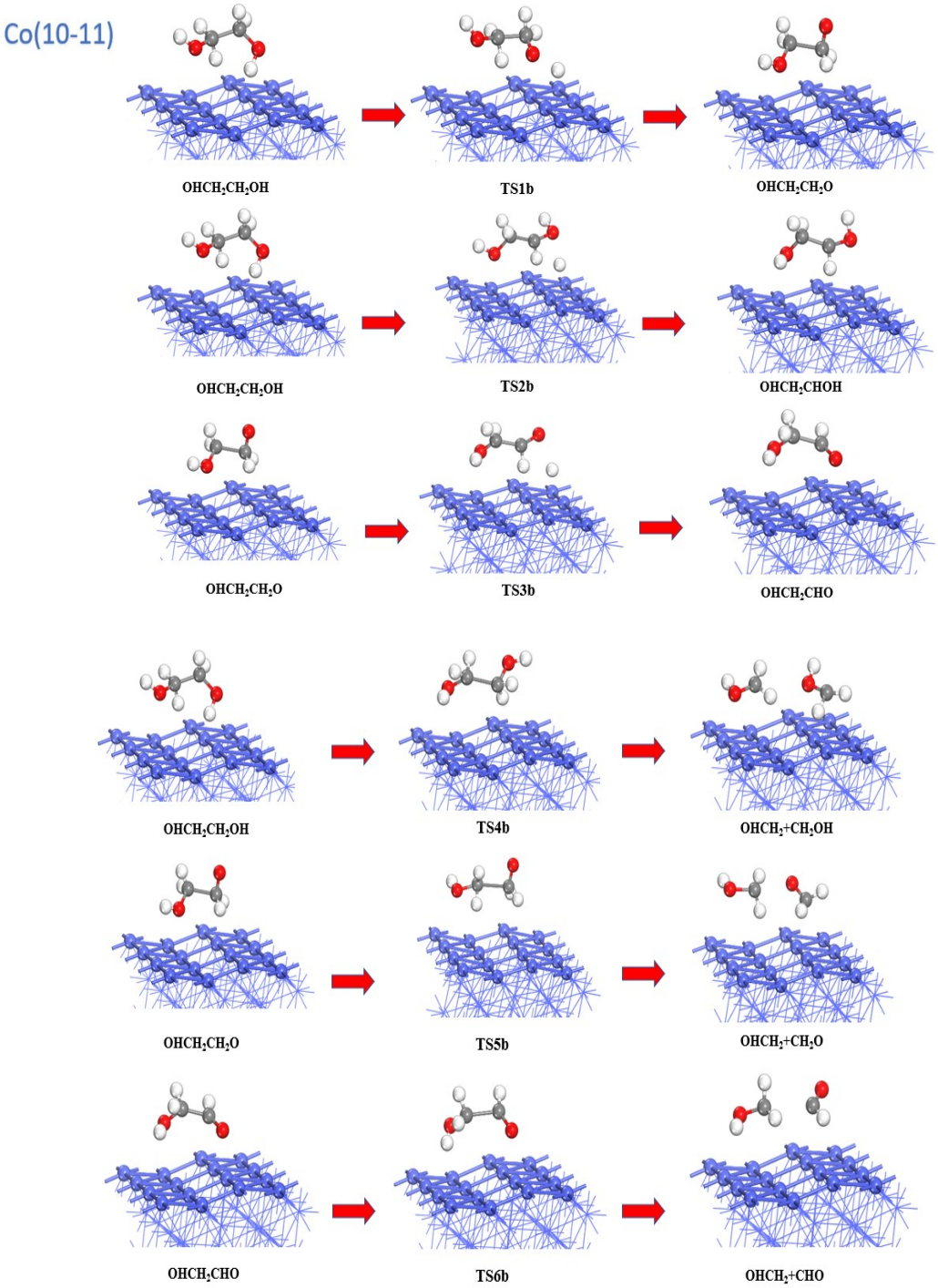
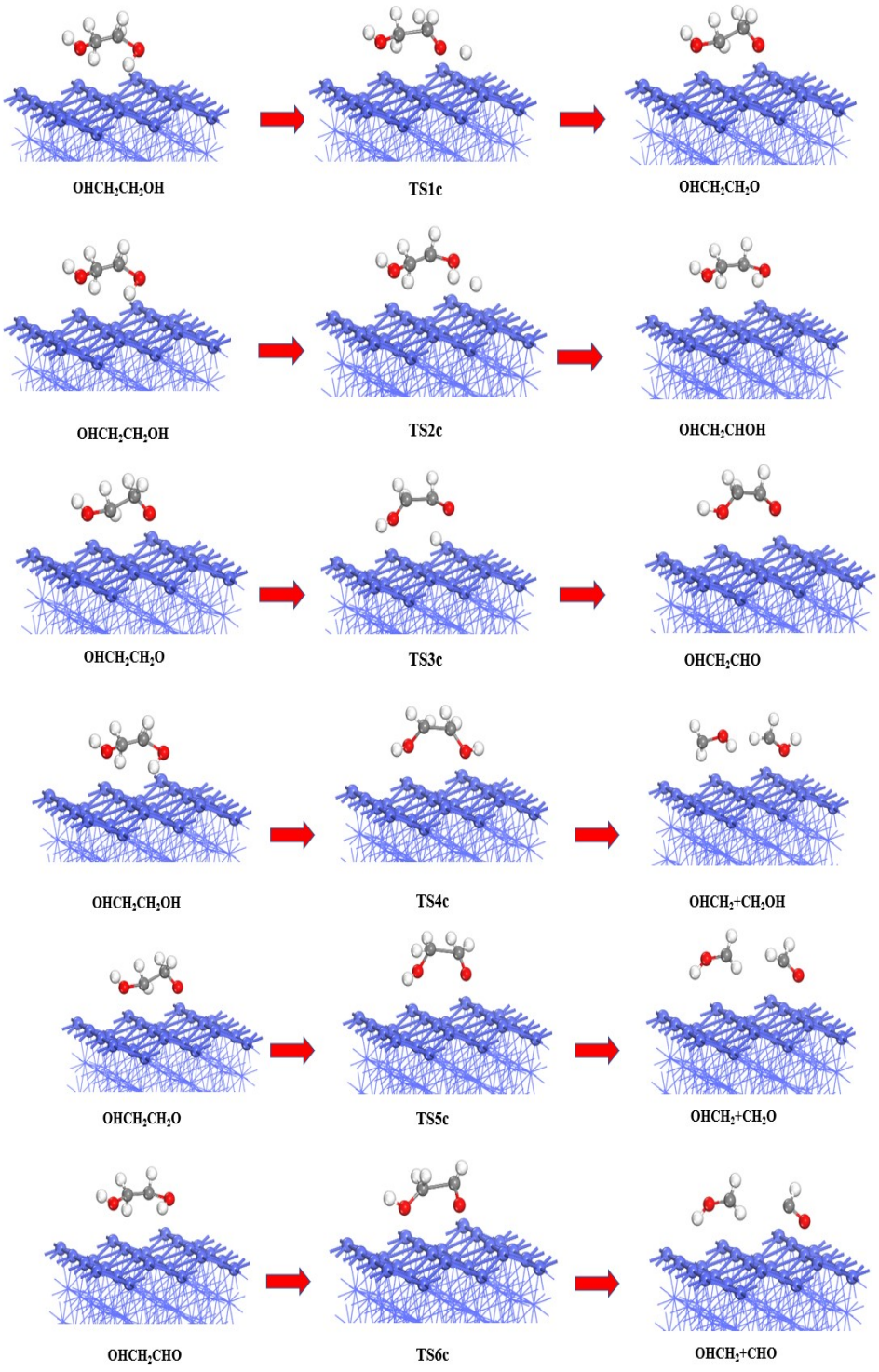
OHCH2CH2O
TS5a
OHCH2+CH2O
OHCH2CHO
TS6a
OHCH2+CHO


Co(10-11)
OHCH2CH2OH
TS1b
OHCH2CH2O
OHCH2CH2OH
TS2b
OHCH2CHOH
OHCH2CH2O
TS3b
OHCH2CHO
OHCH2CH2OH
TS4b
OHCH2+CH2OH
OHCH2CH2O
TS5b
OHCH2+CH2O
OHCH2CHO
TS6b
OHCH2+CHO

Co(10-10)


OHCH2CH2OH
TS1c
OHCH2CH2O
OHCH2CH2OH
TS2c
OHCH2CHOH
OHCH2CH2O
TS3c
OHCH2CHO
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OHCH2+CH2O
OHCH2CHO
TS6c
OHCH2+CHO

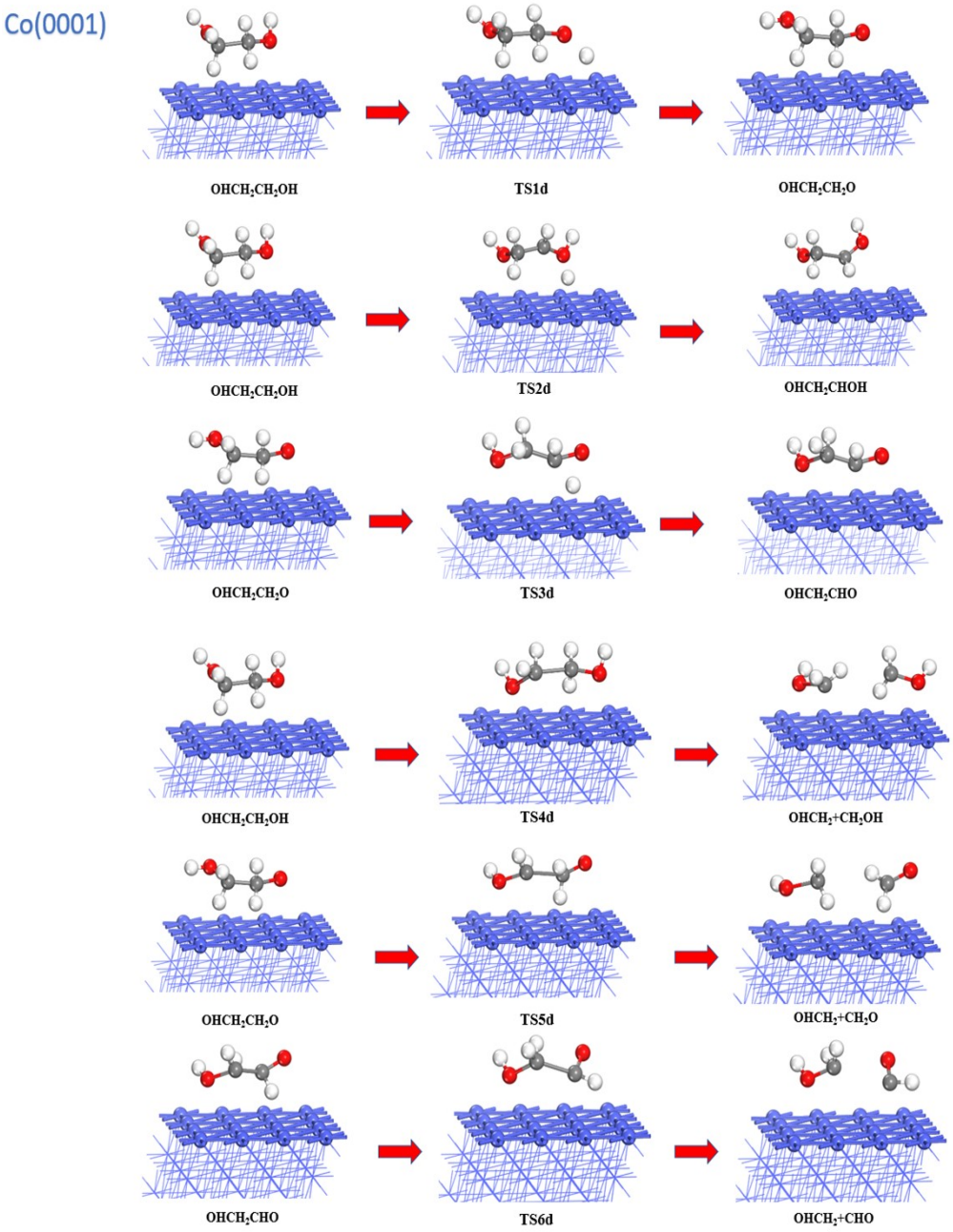

Fig.S2. Images of transition states

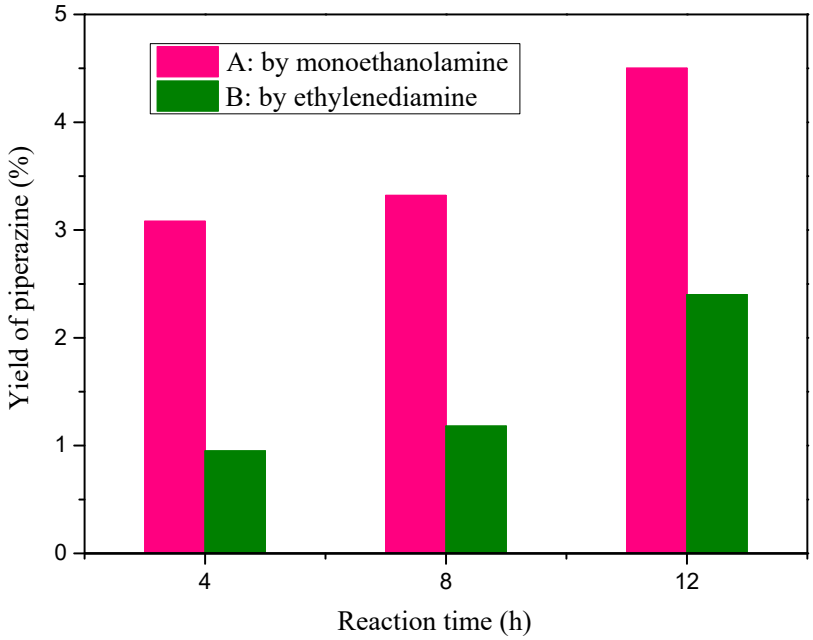

Fig.S3. Comparison of two cyclization pathways to piperazine.

A: Ethanolamine self-condensation reaction: initial hydrogen pressure=3 MPa, $m_{(MEA)}$ =10 g, $m_{(H2O)}$ =70 g, a weight percentage of catalyst (hcp-Co) =10%.

B: Ethylenediamine and ethylene glycol reaction: initial hydrogen pressure=3 MPa, $m_{(EG)}$ =5.08 g, $m_{(EDA)}$ =4.92 g $m_{(H2O)}$ =70 g, a weight percentage of catalyst (hcp-Co) =10%.

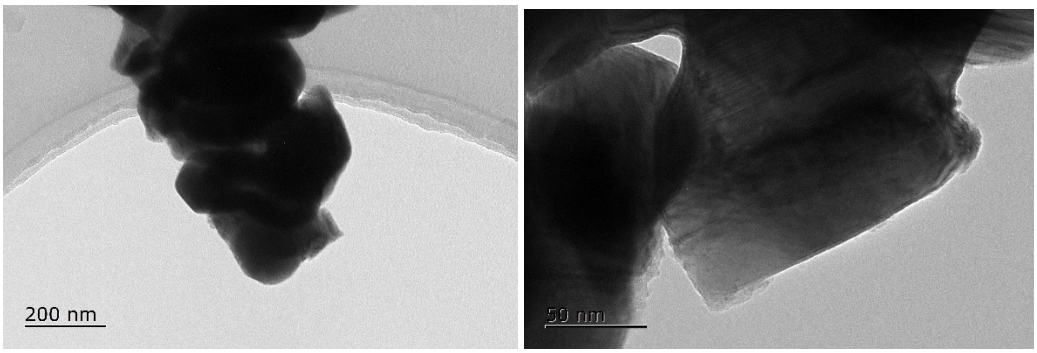

Fig.S4. TEM images of hcp-Co (100-300 nm) catalysts (co-precipitation method).

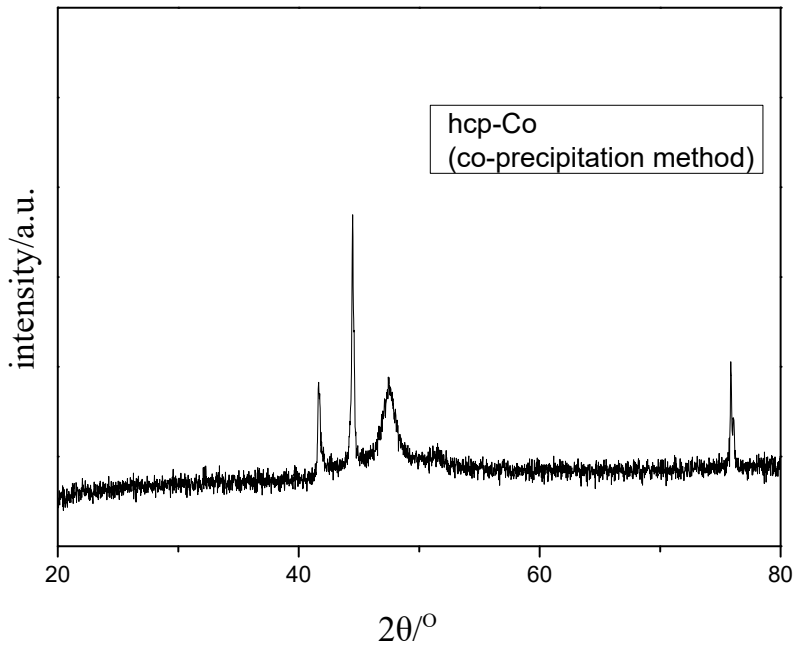

Fig.S5. XRD patterns of hcp-Co (100-300 nm) catalysts (co-precipitation method).

References

1 A. Fischer, M. Maciejewski, T. Bürgi, T. Mallat and A. Baiker, J. Catal., 1999, **183**, 373-383.