## **Supporting Information for**

# Enhanced H<sub>2</sub> Production at Atomic Ni-Ce Interface Following Methanol Steam Reforming

Yaqi Hu,<sup>†</sup> Zhong Liang,<sup>†</sup> Yabin Zhang, Yaping Du,\* and Hongbo Zhang\*

School of Materials Science and Engineering, Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300350, P. R. China

<sup>†</sup>These authors contribute equally.

\*Corresponding Authors:

Yaping Du, ypdu@nankai.edu.cn

Hongbo Zhang, hbzhang@nankai.edu.cn

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## **Results and discussion**

S1 Characterization of the as prepared catalysts



Fig. S1 XRD patterns of the fresh catalysts.



Fig. S2 (i) TEM image and (ii-vi) elemental mappings of NiCe/CN DAC-fresh.





**Fig. S3** Nitrogen adsorption/desorption isotherm plot and pore size distribution obtained from BET measurement of (a, b) NiCe /CN DAC, (c, d) Ni/CN SAC and (e, f) Ni/CeO<sub>2</sub>.

**Table S1.** The EXAFS data fitting results of NiCe /CN DAC

Sample	Coordination	CN	R(Å)	$\sigma^2(*10^{-3}\text{\AA}^2)$	$\Delta E(eV)$	R-factor
_						
Ni foil	Ni-Ni	12	2.48(-0.04)	-	-	0.002
CeO <sub>2</sub>	Ce-O	8	2.32(-0.02)	5.8	-5.3	0.002
	Ce-Ce	12	3.82(-0.09)	6.2	-1.1	0.002
NiCe/CN	Ni-N(O)	5.8	2.04(-0.02)	12.8	-5.3	0.004
	Ce-N(O)	12.1	2.59(-0.09)	15.1	-2.3	0.006

CN is the coordination number; R is interatomic distance;  $\sigma^2$  is Debye-Waller factor;  $\Delta E$  is edge-energy shift; R-factor is used to value the goodness of the fitting.

**Table S2.** The Ni and Ce loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Catalysts	Ni (wt %)	Ce (wt %)
Ni/CN	2.7	-
Ce/CN	-	4.9
NiCe/CN	2.2	4.9



Fig. S4 (a-c) TEM images and (d) Elemental mappings of NiCe/CN DAC-used.



Fig. S5 TG profile of NiCe/CN DAC-used.

S2 Catalytic performance in methanol steam reforming and water-gas shift reaction over NiCe/CN DAC.



**Fig. S6** Mass-dependent activities of NiCe/CN DAC in (a) MSR and (b) WGS reactions. (Reaction conditions of MSR: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, total flow rate =30 ml/min; reaction conditions of WGS: 2 kPa CO, 10 kPa H<sub>2</sub>O, Ar balanced, total flow rate =80 ml/min. Blue  $\triangle$ : 20 mg, yellow  $\bigcirc$ : 50 mg, red  $\bigcirc$ : 100 mg.)



**Fig. S7** Arrhenius plots with H<sub>2</sub> generation rate in (a) MSR and (b) WGS as a function of reversed reaction temperature over various catalysts. (Reaction conditions of MSR: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, GHSV=19099 h<sup>-1</sup>; Reaction conditions of WGS: 2 kPa CO, 10 kPa H<sub>2</sub>O, Ar balanced, GHSV=10186 h<sup>-1</sup>. Red ○: NiCe/CN DAC, brown  $\nabla$ : NiLa/CN DAC, sapphire  $\diamond$ : NiY/CN DAC, green  $\bullet$ : Ni/CN SAC, purple  $\Delta$ : Ce/CN SAC, yellow  $\triangleleft$ : Ni/CeO<sub>2</sub>, blue  $\triangleright$ : Pt/Al<sub>2</sub>O<sub>3</sub>)

 Table S3. The apparent activation energies of NiCe/CN DAC and reference samples

 in MSR and WGS.

Catalysts	Ea of MSR (kJ/mol)	Ea of WGS (kJ/mol)
NiCe/CN DAC	63.5	60.5
NiLa/CN DAC	73	65.4
NiY/CN DAC	82.4	77.1
Ni/CN SAC	76.6	79.7
Ce/CN SAC	189.4	194.2
Ni/CeO <sub>2</sub>	69.6	70.1
Pt/Al <sub>2</sub> O <sub>3</sub>	75.4	67.3

Cat	tolvata	Ponction oor	Conv.	CO Selec.	TOR	Dof	
Ca	larysis	Keaction con	lations	(%)	(%)	$(\mu mol_{H2}/g_{cat.}/s)$	Kel.
2% P	t/α-MoC	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:3 100 mg, 50 ml	463 K, 2 MPa	-	0.06	129.6	[1]
2% N	li/α-MoC	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:1 100 mg, 50 ml	513 K, 10 h 2 MPa	-	0.7	171	[2]
7% Ni	Cu-3% /Al <sub>2</sub> O <sub>3</sub>	$n_{MeOH}: n_{H2O} = 1:1.7$ 3 g	498 K, 101.325 kPa	94	-	-	[3]
Ni	/CeO <sub>2</sub>	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:3	573 K, 101.325 kPa	68	20	-	[4]
NiA	Al-LDH	100 mg	613 K, 101.325 kPa	16.1	6.4	47	[5]
( Pd/Z	).1% ZnAl <sub>2</sub> O <sub>4</sub>	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:1.1 300 mg	523 K, 101.325 kPa	38	3	11.4	[6]
InPe	d/In <sub>2</sub> O <sub>3</sub>	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:1 1g	573 K, 101.325 kPa	26	1	-	[7]
Ru	1/CeO2	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:3 100 mg	623 K, 101.325 kPa	25.6	2.2	38.8	[8]
Cu/Zı	nO/Al <sub>2</sub> O <sub>3</sub>	$n_{MeOH}: n_{H2O}$ =1:1.3 100 mg	498 K, 1bar	67	70	-	[9]
Ni	Ce/CN	n <sub>MeOH</sub> : n <sub>H2O</sub> =1:16 100 mg	513 K, 101.325 kPa	99.1	0.8	6.5	This wor k

**Table S4.** Catalytic performance comparison of methanol reforming at variousreaction conditions on a series of catalysts.



Fig. S8 Temperature-dependent activities and carbon product selectivities of NiCe/CN DAC. (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, GHSV=318 h<sup>-1</sup>)

![](_page_8_Figure_2.jpeg)

**Fig. S9** The long-term stability of NiCe/CN DAC in MSR. (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623 K, GHSV=318 h<sup>-1</sup>)

#### S3 Quasi-in-situ XPS characterization

![](_page_9_Figure_1.jpeg)

**Fig. S10** Ni 2p XPS spectra of the Ni/CN SAC after reduction (i: 10 % H<sub>2</sub>/Ar, 623 K, 2 h, 50 mL/min), under MD condition for 1 h (ii: 1 kPa CH<sub>3</sub>OH, Ar balanced, 623 K, 30 mL/min) and under MSR condition for 1 h (iii: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623 K, 30 mL/min).

![](_page_9_Figure_3.jpeg)

**Fig. S11** (a) Ni 2p XPS spectra and (b) Ce 3d XPS spectra of the Ni/ CeO<sub>2</sub> after reduction (i: 10 %  $H_2/Ar$ , 623 K, 2 h, 50 mL/min), under MD condition for 1 h (ii: 1 kPa CH<sub>3</sub>OH, Ar balanced, 623 K, 30 mL/min) and under MSR condition for 1 h (iii: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623 K, 30 mL/min).

Catalysts		N	Ni <sup>0</sup>		Ni <sup>2+</sup>		Ni <sup>3+</sup>	
		BE	Content	BE	Content	BE	Content	
	i	-	-	855.8	82.6%	858.8	17.4%	
Ni/CN	ii	853.0	5.8%	855.4	72.5%	858.0	21.7%	
	iii	853.7	19.9%	855.4	56.8%	857.7	23.3%	
	i	-	-	854.9	87.0%	857.2	13.0%	
NiCe/CN	ii	852.3	9.2%	854.4	70.9%	856.7	19.9%	
	iii	852.2	8.1%	854.4	74.1%	856.7	17.8%	
Ni/CeO <sub>2</sub>	i	853.6	23.2%	855.5	66.1%	857.2	10.7%	
	ii	852.6	10.5%	854.4	80.6%	857.2	8.9%	
	iii	852.7	10.9%	854.4	78.2%	856.8	10.9%	

Table S5. X-ray photoelectron spectroscopy analysis results of Ni  $2p_{3/2}$ .

i (Reduction): 10 % H<sub>2</sub>/Ar, 623 K, 2 h, 50 mL/min

ii (MD): 1 kPa CH<sub>3</sub>OH, Ar balanced, 623 K, 1 h, 30 mL/min

iii (MSR): 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623 K, 1 h, 30 mL/min

Table S6. X-ray photoelectron spectroscopy analysis results of Ce 3d.

Catalysts			Area ratio of peaks					Average
		$u_0 v_0$	u v	u' v'	u" v"	u''' v'''		valance
	i	0.25	1.69	1.02	0.97	1.49	23.4%	3.77
NiCe/CN	ii	0.53	1.20	1.55	0.46	0.78	45.9%	3.54
	iii	0.64	1.17	1.58	0.41	0.59	50.6%	3.49
Ni/CeO <sub>2</sub>	i	0.37	1.17	1.06	1.1	1.69	26.5%	3.74
	ii	0.69	1.20	1.69	0.59	1.00	46.0%	3.54
	iii	0.71	1.10	1.69	0.51	0.88	49.1%	3.51

i (Reduction): 10 % H<sub>2</sub>/Ar, 623 K, 2 h, 50 mL/min

ii (MD): 1 kPa CH<sub>3</sub>OH, Ar balanced, 623 K, 1 h, 30 mL/min

iii (MSR): 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623 K, 1 h, 30 mL/min

S4 Steady-state isotopic transient kinetic analysis (SSITKA) combined with *insitu* FTIR measurements over NiCe/CN DAC

![](_page_11_Figure_1.jpeg)

Fig. S12 Schematic diagram of fitting the IR spectra collected at 50 min in Fig. 4a.

![](_page_11_Figure_3.jpeg)

**Fig. S13** IR spectra of NiCe/CN DAC recorded at 623 K during a SSITKA experiment from the initial flow made of 10 kPa D<sub>2</sub>O in Ar to a similar unlabeled (10 kPa H<sub>2</sub>O) gas-mixture. (Total flow rate: 50 mL/min)

![](_page_12_Figure_0.jpeg)

**Fig. S14** IR spectra of NiCe/CN DAC recorded at 623 K during a SSITKA experiment from the initial flow made of 2kPa CH<sub>3</sub>OH and 10 kPa H<sub>2</sub>O in Ar to a similar labeled (2kPa CD<sub>3</sub>OD and 10 kPa H<sub>2</sub>O) gas-mixture. (Total flow rate: 50 mL/min)

![](_page_12_Figure_2.jpeg)

**Fig. S15** IR spectra of NiCe/CN DAC recorded at 623 K during a SSITKA experiment from the initial flow made of 2kPa CH<sub>3</sub>OH and 15 kPa H<sub>2</sub>O in Ar to a similar labeled (2kPa CD<sub>3</sub>OD and 15 kPa H<sub>2</sub>O) gas-mixture. (Total flow rate: 50 mL/min)

S5 Exclusion of external and internal diffusion limitation

![](_page_13_Figure_1.jpeg)

**Fig. S16** (a) Change the gas hourly space velocity (GHSV) over 2% NiCe/CN DAC to exclude the internal diffusion resistance (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623K); (b) Serial loading of x wt% NiCe/CN DAC (x=0.1, 0.5, 1, 2) to exclude the external diffusion resistance (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 623K, GHSV=19099 h<sup>-1</sup>).

#### S6 The involvement of WGS within the MSR

In general, MSR consists of MD and WGS.	
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	(S1)
$CH_3OH \rightarrow CO + 2H_2$	(82)
$CO + H_2 O \rightarrow CO_2 + H_2$	(\$3)

We set the reaction rate of MD as E1, and the reaction rate of WGS is set as E2. Then, the formation rate of  $H_2$  and CO are respectively equal to,

$$f_{H_2} = 2E1 + E2$$
 (S4)

$$f_{CO} = E1 - E2 \tag{S5}$$

Then we define the formation ratio between  $H_2$  and CO as  $\eta\colon$ 

$$\eta = \frac{f_{H_2}}{f_{CO}} = \frac{2E1 + E2}{E1 - E2}$$
(S6)

And  $\eta$  can also be used to describe the involvement of WGS in the overall MSR. Methanol decomposes to form CO and H<sub>2</sub>. If no WGS occurs at all, then E2 is equal to 0 and  $\eta$  is calculated as 2. Once WGS occurs, CO will be consumed and H<sub>2</sub> will generate at the same time, in this case, the value of  $\eta$  should be greater than 2 and increase with the increased involvement of WGS. Until all of the CO produced by MD participates in WGS, so E1 is equal to E2, then  $\eta$  goes to infinity. Therefore, the reaction degree of WGS and MD can be judged according to the value of  $\eta$ .

Then we define the reaction rate ratio of MD to WGS as  $\varepsilon$ :

$$\varepsilon = \frac{r_{MD}}{r_{WGS}} = \frac{E1}{E2} \tag{S7}$$

substitute Eq. S13 into Eq. S14,

$$\varepsilon = \frac{\eta + 1}{\eta - 2} \tag{S8}$$

If MD is dominant and WGS almost does not occur, then  $\varepsilon$  will tend to infinity. With the increased involvement of WGS,  $\varepsilon$  will gradually decrease until all CO produced by MD participates in WGS, that is, E1 is equal to E2, at which time  $\varepsilon$  has a minimum value of 1.

In general, as shown in **Fig. S16** and **Fig. S17**, with the increase of pressure of  $H_2O$  or conversion, whether from the increasing CO selectivity or the trend of increasing  $\eta$  and decreasing  $\varepsilon$ , it indicates that the involvement of WGS within the whole reaction process is gradually increasing.

![](_page_14_Figure_7.jpeg)

Fig. S17 Influence of  $H_2O$  pressure on the involvement of WGS. (a)  $H_2O$  pressuredependent activities and (b) carbon product selectivities of MSR on 1% NiCe/CN DAC (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 2-30 kPa H<sub>2</sub>O, Ar balanced, 623 K)

![](_page_15_Figure_0.jpeg)

**Fig. S18** Influence of methanol conversion on the involvement of WGS. (a) Activities as a function of conversion and (b) trend of carbon product selectivities with the conversion of MSR on 2% NiCe/CN DAC (Reaction conditions: 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O, Ar balanced, 423-513 K, GHSV=318 h<sup>-1</sup>).

#### S7 Kinetic pressure dependence study

![](_page_15_Figure_3.jpeg)

**Fig. S19** (a) H<sub>2</sub> formation rate as functions of CO<sub>2</sub> pressures ( $\bigtriangledown$ : 1-50 kPa CO<sub>2</sub>, 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O) and (b) CH<sub>3</sub>OH consumption rate as a function of H<sub>2</sub> pressures ( $\diamond$ : 3-80 kPa H<sub>2</sub>, 1 kPa CH<sub>3</sub>OH, 16.02 kPa H<sub>2</sub>O) of MSR reaction at different temperature and atmospheric pressure.

![](_page_16_Figure_0.jpeg)

**Fig. S20** H<sub>2</sub> formation rate as functions of CO<sub>2</sub> pressures (olive  $\diamond$ : 0.5-40 kPa CO<sub>2</sub>, 2 kPa CO, 10 kPa H<sub>2</sub>O), H<sub>2</sub>O (red  $\bigcirc$ : 2-60 kPa H<sub>2</sub>O, 2 kPa CO), and CO pressures (cyan  $\nabla$ : 0.2-10 kPa CO, 10 kPa H<sub>2</sub>O) and CO<sub>3</sub> formation rate as a function of H<sub>2</sub> pressures (blue  $\triangle$ : 2-30 kPa H<sub>2</sub>, 2 kPa CO, 10 kPa H<sub>2</sub>O) of WGS reaction at 573 K and atmospheric pressure.

#### S8 Proposed mechanism and complete derivation of the rate expression for MSR.

Steps	Constant
CH <sub>3</sub> OH + 2 * → CH <sub>3</sub> O* + H*	<b>K</b> <sub>1</sub>
$CH_3O^* + * \longrightarrow CH_2O^* + H^*$	$\mathbf{k}_2$
CH <sub>2</sub> O* + * → CHO* + H*	$\mathbf{K}_3$
CHO* + * CO* + H*	$\mathbf{K}_4$
CO* <del>&lt;  ←</del> CO+*	<b>K</b> <sub>5</sub>
$H_2O + O_V \implies H_2O_L$	$\mathbf{K}_{6}$
$H_2O_L + * \implies HO_L + H^*$	<b>K</b> <sub>7</sub>
$HO_L + * \longrightarrow O_L + H^*$	<b>k</b> <sub>8</sub>
$CO* + O_L \implies COO_L + *$	K <sub>9</sub>
$COO_L \iff CO_2 + O_V$	<b>K</b> <sub>10</sub>
$2 \text{ H}^* \implies \text{H}_2 + 2 *$	K <sub>11</sub>

Scheme S1. Proposed mechanism of MSR on 1% NiCe/CN DAC.

#### **S8.1.** Complete derivation of the rate expression for MD.

#### S8.1.1 CH<sub>3</sub>OH dehydrogenation as the KRS.

If  $CH_3OH$  dehydrogenation to form  $CH_3O^*$  is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_1 [CH_3 OH] [*]^2}{[L_{Ni}] [L_{Ce}]}$$
(S9)

After considering about the quasi-equilibrated (QE) assumption on CH<sub>3</sub>OH adsorption, CO and CO<sub>2</sub> desorption,  $H_2O$  activation,  $H_2$  and O<sub>L</sub>H formation:

$$[CH_3O*] = \frac{K_1[CH_3OH][*]^2}{[H*]}$$
(S10)

$$[CO*] = \frac{[CO][*]}{K_5}$$
(S11)

$$[COO_L] = \frac{[CO_2][O_V]}{K_{10}}$$
(S12)

$$[H_2 O_L] = K_6 [H_2 O] [O_V]$$
(S13)

$$[H*] = \frac{[H_2]^{\frac{1}{2}}[*]}{K_{11}^{\frac{1}{2}}}$$

$$K_7[H_2O_1][*]$$
(S14)

$$[HO_L] = \frac{m_{7L}m_{2}O_{L}1[*]}{[H*]}$$
(S15)

substitute Eq. S14 into Eq. S10,

1

$$[CH_{3}O*] = \frac{K_{1}K_{11}^{\frac{1}{2}}[CH_{3}OH][*]}{[H_{2}]^{\frac{1}{2}}}$$
(S16)

and substitute Eq. S13, Eq. S14 into Eq. S15,

$$[HO_L] = \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 O][O_V]}{[H_2]^{\frac{1}{2}}}$$
(S17)

The expression of surface intermediates would be simplified as:  $[L] = ([*] + [H*] + [CO*] + [CH_3O*]) \cdot ([O_v] + [COO_L] + [HO_L])$ 

$$= [*][0_{v}](1 + \frac{[H_{2}]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[CO]}{K_{5}} + \frac{K_{1}K_{11}^{\frac{1}{2}}[CH_{3}OH]}{[H_{2}]^{\frac{1}{2}}})(1 + \frac{[CO_{2}]}{K_{10}} + \frac{K_{6}K_{7}K_{11}^{\frac{1}{2}}[H_{2}O]}{[H_{2}]^{\frac{1}{2}}})$$
(S18)

The reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_1[CH_3OH]}{(1 + \frac{[H_2]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[CO]}{K_5} + \frac{K_1K_{11}^{\frac{1}{2}}[CH_3OH]}{[H_2]^{\frac{1}{2}}})(1 + \frac{[CO_2]}{K_{10}} + \frac{K_6K_7K_{11}^{\frac{1}{2}}[H_2O]}{[H_2]^{\frac{1}{2}}})$$

(S19)

## S8.1.2. CH<sub>3</sub>O\* dehydrogenation as the KRS.

If  $CH_3O^*$  dehydrogenation to form  $CH_2O^*$  is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_2 [CH_3O*][*]}{[L_{Ni}][L_{Ce}]}$$

(S20)

The expression of surface intermediates would be same as above, so the reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_2 K_1 K_{11}^{\frac{1}{2}} [CH_3 OH]}{[H_2]^{\frac{1}{2}} (1 + \frac{[H_2]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[CO]}{K_5} + \frac{K_1 K_{11}^{\frac{1}{2}} [CH_3 OH]}{[H_2]^{\frac{1}{2}}})(1 + \frac{[CO_2]}{K_{10}} + \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 O]}{[H_2]^{\frac{1}{2}}})$$

(S21)

## S8.1.3. CH<sub>2</sub>O\* dehydrogenation as the KRS.

If  $CH_2O^*$  dehydrogenation to form CHO\* is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_3 [CH_2 O *][*]}{[L_{Ni}] [L_{Ce}]}$$

(S22)

After considering about the quasi-equilibrated (QE) assumption on  $CH_3O^*$  dehydrogenation to form  $CH_2O^*$ :

$$[CH_2O*] = \frac{K_2[CH_3O*][*]}{[H*]} = \frac{K_1K_2K_{11}[CH_3OH][*]}{[H_2]}$$
(S23)

The expression of surface intermediates would be same as above, so the reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_3 K_1 K_2 K_{11} [CH_3 OH]}{[H_2] (1 + \frac{[H_2]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[CO]}{K_5} + \frac{K_1 K_{11}^{\frac{1}{2}} [CH_3 OH]}{[H_2]^{\frac{1}{2}}})(1 + \frac{[CO_2]}{K_{10}} + \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 O]}{[H_2]^{\frac{1}{2}}})$$

(S24)

#### **S8.1.4.** CHO\*<sub>I</sub> dehydrogenation as the KRS.

If CHO\* dehydrogenation to form CO\* is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_4 [CHO *][*]}{[L_{Ni}][L_{Ce}]}$$
(S25)

After considering about the quasi-equilibrated (QE) assumption on  $CH_2O^*$  dehydrogenation to form CHO\*:

$$[CHO*] = \frac{K_3[CH_2O*][*]}{[H*]} = \frac{K_1K_2K_3K_{11}^{\frac{3}{2}}[CH_3OH][*]}{[H_2]^{\frac{3}{2}}}$$

(S26)

The expression of surface intermediates would be same as above, so the reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_4 K_1 K_2 K_3 K_{11}^{\frac{3}{2}} [CH_3 OH]}{[H_2]^{\frac{3}{2}} (1 + \frac{[H_2]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[CO]}{K_5} + \frac{K_1 K_{11}^{\frac{1}{2}} [CH_3 OH]}{[H_2]^{\frac{1}{2}}})(1 + \frac{[CO_2]}{K_{10}} + \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 O]}{[H_2]^{\frac{1}{2}}})$$

(S27)

The desorption of CO adsorbed may not be kinetically relevant step, due to the absence of KIE of H-D exchange.

## S8.2. Complete derivation of the rate expression for WGS.

#### S8.2.1 Dissociatively adsorption of H<sub>2</sub>O as the KRS.

If H<sub>2</sub>O<sub>L</sub> dehydrogenation to form HO<sub>L</sub> is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_7 [H_2 O_L][*]}{[L_{Ni}] [L_{Ce}]}$$
(S28)

The expression of surface intermediates would be same as above, so the reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_7 K_6 [H_2 0]}{\left(1 + \frac{[H_2]^2}{K_{11}^{\frac{1}{2}}} + \frac{[C0]}{K_5} + \frac{K_1 K_{11}^{\frac{1}{2}} [CH_3 0H]}{[H_2]^{\frac{1}{2}}}\right)\left(1 + \frac{[C0_2]}{K_{10}} + \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 0]}{[H_2]^{\frac{1}{2}}}\right)$$

(S29)

#### S8.2.2. Rupture of O<sub>L</sub>-H bond as the KRS.

If rupture of O<sub>L</sub>H to form O<sub>L</sub> is assumed to be KRS, the reaction rate would be expressed as:

$$\frac{r}{[L]} = \frac{k_8 [HO_L][*]}{[L_{Ni}][L_{Ce}]}$$

(S30)

The expression of surface intermediates would be same as above, so the reaction rate could be finally expressed as:

$$\frac{r}{[L]} = \frac{k_8 K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 0]}{[H_2]^{\frac{1}{2}} (1 + \frac{[H_2]^{\frac{1}{2}}}{K_{11}^{\frac{1}{2}}} + \frac{[C0]}{K_5} + \frac{K_1 K_{11}^{\frac{1}{2}} [CH_3 0H]}{[H_2]^{\frac{1}{2}}})(1 + \frac{[C0_2]}{K_{10}} + \frac{K_6 K_7 K_{11}^{\frac{1}{2}} [H_2 0]}{[H_2]^{\frac{1}{2}}})$$
(S31)

According to  $r_{H_2} = r_{MD} + r_{WGS}$ , add the hypothetical expressions of the H<sub>2</sub> formation rate in MD and WGS corresponding to different KRS, and by assuming different species as MASIs, only the expression about considering the rupture of C-H bond in CH<sub>3</sub>O\* and the rupture of O<sub>L</sub>-H bond in hydroxyl group to be KRS (Eq. 3) matches the trends observed in previous pressure study (Fig. 5). The expression 21

shows first or zeroth order dependence of  $CH_3OH$  pressures, first order or zeroth order dependence of  $H_2O$  pressures, zeroth order or negative first order dependence of CO pressures, zeroth order or negative first order dependence of  $CO_2$  pressures, zeroth order or negative first order dependence of  $H_2$  pressures, zeroth order or negative first order dependence of  $H_2$  pressures.

The formation and desorption of CO<sub>2</sub> species may not be kinetically relevant steps, due to the absence of KIE of H-D exchange.

S9 Isotope tracing and kinetic isotope effects assessment.

![](_page_21_Figure_3.jpeg)

**Fig. S21**  $H_2$  formation rates for MD at 623 K (1 kPa isotopes of CH<sub>3</sub>OH, Ar balanced, GHSV=19099 h<sup>-1</sup>) as a function of time.

![](_page_21_Figure_5.jpeg)

**Fig. S22**  $H_2$  formation rates for WGS at 623 K (10 kPa isotopes of  $H_2O$ , 2 kPa CO, Ar balanced, GHSV=19099 h<sup>-1</sup>) as a function of time.

![](_page_22_Figure_0.jpeg)

Fig. S23  $H_2$  formation rates for MSR at 623 K (1 kPa isotopes of  $CH_3OH$ , 2 kPa isotopes of  $H_2O$ , Ar balanced, GHSV=19099 h<sup>-1</sup>) as a function of time.

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