Supplementary information for

Computational Study of the Evolution of Ni-Based Catalysts during the Dry Reforming of Methane

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A. Model construction of the intermediate models of the partially oxidized (O/Ni) and partially

carburized (C/Ni) Ni catalysts

- 1. The O/Ni models
 - Oxidation route

First, for the *oxidation process* (route 1) depicted schematically in Figure 4(a), it is assumed that the reaction follows the Cabrera-Mott model describing the formation of the metal oxide[1]. The initial surface is depicted by pure Ni (model a1 in Figure 4(a)) and as the oxidation proceeds, the surface is oxidized from the top layer down to the lower ones (model a2 in Figure 4(a)) resulting in the final system having oxide over metallic Ni (model a3 in Figure 4(a)). Note that if the oxidation is complete, the resulting structure (model a3) will be a pure oxide. However, whether or not the oxidation is complete, we chose to represent only the top portion of the oxide represented by the slab model of pure Ni oxide. This is because the oxide could form quickly during the reaction and we assume only the top oxide layer would play a major role in the surface reaction. The oxidation process is studied on the Ni(100), where the complete oxidation would lead to the NiO(100) since both surfaces (metal and oxide) have the analogous (100) surface type. This means that if all O atoms were removed from NiO(100) the resulting structure would be Ni(100). This NiO(100) facet was investigated since we found that it has highly coke-resistant as confirmed by its high E_a for C formation via both CH* and CO* species. Therefore, the calculation aims to determine if there is a minimum number of oxide layers that makes the partially oxidized metallic surface exhibiting an oxide-like behavior with respect to coking (e.g., showing similar carbon adsorption energy to a pure NiO(100) surface). If this is the case, then a complete oxide phase in the catalyst would not be necessary for achieving a high coke-resistant property similar to the pure NiO(100). For this reason, the starting structure (model a1) is modelled by the Ni(100) slab model, while multiple intermediate models (model a2) are the partially oxidized Ni(100) constructed as a thin NiO(100) film with various thicknesses on top of Ni(100) slab models. and the final structure (model a3) is the NiO(100) slab model. The optimized structures of this process are shown in Figure 5, which are initial (model 0), intermediate (models 1, 2, 3, 4), and final (model 5) stages.

The construction of the model describing the oxidation of the metallic Ni is illustrated in Figure S1. First of all, although the process occurs in the direction from left to right, the initial structure to start with is system number 5, the pure 5-layer NiO(100) slab model which is cleaved from the optimized NiO bulk crystal structure. System number 5 is optimized with the setup stated in the "Method" section in the main text. As this calculation is run in VASP, the ISIF tag which designates whether the stress tensor is calculated or not and whether any degree-of-freedom is allowed to change in the relaxation is adjusted in the following manner. Starting with the unoptimized structure, the ISIF is set to 2 calculating both the force and stress tensors, while cell shape and volume are fixed, letting only the ionic positions to change but still fixing the cell volume.

In the final step, ISIF is set to 3 to allow cell volume to change, where at this point the system is completely relaxed as confirmed by the energy decrease of the system. Due to ISIF=3, the vacuum in c-axis will decrease, so we re-constructed the vacuum again to be 10 Å in each slab and optimized with ISIF = 2 to obtain the total energy of the system. Note that for volume changes relaxation the cutoff energy is increased in order to avoid the incorrect calculation of the stress tensor ([1] <u>http://cms.mpi.univie.ac.at/vasp/guide/node161.html#pullay</u>). Next, for the construction of systems number 5, 4, 3, 2 and 1. The oxygen atom in a system number 6 is removed from the bottom layer step-wise, while all atoms were relaxed followed by the optimization by the mentioned step using ISIF = 2 \rightarrow ISIF = 4 \rightarrow ISIF = 3.



(atomic color label: grey = Nickel, red = Oxygen)

Figure S1. the unit cell of systems in the *oxidation route*, where the formula is $(0) = Ni_{40} / (1) = Ni_{40}O_8 / (2) = Ni_{40}O_{16} / (3) = Ni_{40}O_{24} / (4) = Ni_{40}O_{32} / (5) = Ni_{40}O_{40}$.

In addition, A. Rohrbach, J. Hafner, G. Kresse, (Molecular adsorption on the surface of strongly correlated transition-metal oxides: A case study for CO/NiO(100), Phys Rev B, 69 (2004) 075413.) showed that the concentration has small effects on the adsorption energy. Thus, for our modelling, the selection of the (2x2) model unit cells is estimated to be within the reliable range.

• Deoxygenation route

The *deoxygenation process* (route 4) was described as the deoxygenation of the top oxide layer of Ni, in which the removal of the oxygen atoms initiates at the top surface before proceeding to the lower layers. As seen from Figure 4 (a), the initial structure of this route (model a3) is the Ni core covered by its oxide. According to this, only the oxide portion is considered for the deoxygenation process, and the inner core of Ni is not included in the model. As a result, the first structure for this deoxygenation route is represented by a NiO(100) slab model, where the bottom layer of the slab model is fixed to the lattice parameter of the bulk NiO[2], while the intermediate models consisted of top layers of pure Ni of different thicknesses on top of the NiO. Note that during the optimization, only the bottom Ni and O layers are fixed while the rest of the atoms are relaxed, and the cell shape and size are allowed to change. The optimized models for this process are illustrated in Figure 5, which are initial (model 5), intermediate (models 6, 7, 8, 9), and final (model 0) stages.

Like in the case of the oxidation route, this deoxygenation also starts from the pure 5-layer NiO(100) slab model denoted as system number 5 in Figure S2. However, the slab models in system number 6, 7, 8 and 9 have the bottom 2 layers (Ni and O layers) fixed to the lattice parameter of the optimized NiO bulk and to imitate the situation where the prepared catalyst in the reduction step undergoes the reduction resulting in a metallic surface with a NiO core, the same step-wise removal of the oxygen but now from the top surface is carried out, where the same procedure using ISIF $2 \rightarrow 4 \rightarrow 3$ is applied.



(atomic color label: grey = Nickel, red = Oxygen)

Figure S2. the unit cell of systems in the *deoxygenation route*, where the formula is $(5) = Ni_{40}O_{40}$ // (6) = $Ni_{40}O_{32}$ // (7) = $Ni_{40}O_{24}$ // (8) = $Ni_{40}O_{16}$ // (9) = $Ni_{40}O_{8}$ // (0) Ni_{40} .

Computational details for oxidation and deoxygenation routes

- \circ Number of the layers in the slab model = 5 NiO layers
- \circ ENCUT = 450 eV
- KPOINTS = Monkhorst-Pack [3] grid of 4x4x1 sampling
- Lattice parameter = 4.168 Å which is in good agreement with Madelung et al.[2] of 4.1705 at zero Kelvin

2. The C/Ni models

Carburization route

For the *carburization* process (route 2), as the carbide formation begins, the adsorbed carbon atoms on the top metallic Ni surface (model b1 Figure 4 (b)) will start to diffuse down to the lower Ni layer forming carbide layers and ultimately arrive at the complete carbide phase[10]. It is assumed that the carbon atoms adsorbed on the top surface always saturate the surface so that the carbon diffusion into the Ni layer is continuous and the formation of carbide layer propagates down to the bottom Ni layer which ended up as either complete Ni carbide or with the remaining Ni core (model b3 Figure 4 (b)). We model the starting system as the pure Ni metal. with the initial configuration exposing the Ni(111) facet, while the intermediate models are the partially carburized Ni(111) which has the carbide facet of Ni₃C(001) as the top layer, and the final configuration is the pure carbide $Ni_3C(001)$ structure. The reason to model (111) facet type in this process is that as the Ni(111) is the most coke-resistant surface among the investigated Ni metallic surfaces. This choice would allow us to estimate the maximum thickness of carbide layers formed on the metallic Ni(111) before this partially carburized surface changes from metallic-like to carbide-like with respect to coke formation. Thus, Ni(111) and Ni₃C(001) were chosen as starting and final structures since they are analogous surfaces, where if all C atoms are removed from $Ni_3C(001)$ the resulting structure would be Ni(111). The optimized models of each stage are shown in Figure 6.

The model construction illustrating the carburization of the metallic Ni is depicted in Figure S3. The process occurs in the direction from the left to right but again the initial structure is the pure 7-layer Ni₃C(001) slab model which is cleaved from the optimized Ni₃C bulk described in the "Method" section in the paper. For the construction of system number 6, 5, 4, 3, 2, 1 and 0. The carbon atom is removed step-wise from the bottom layer, while all atoms are relaxed and followed by the optimization via the mentioned step of ISIF = 2 \rightarrow ISIF = 4 \rightarrow ISIF = 3.



(atomic color label: grey = Nickel, brown = Carbon)

Figure S3. the unit cell of systems in the *carburization route*, where the formula is $(0) = Ni_{84} / (1) = Ni_{84}C_4 / (2) = Ni_{84}C_8 / (3) = Ni_{84}C_{12} / (4) = Ni_{84}C_{16} / (5) = Ni_{84}C_{20} / (6) = Ni_{84}C_{24}$.

Computational details for the carburization route

- Number of layers in the slab model = $7 \text{ Ni}_3\text{C}$ layers
- \circ ENCUT = 450 eV
- KPOINTS = Monkhorst-Pack [3] grid of 4x4x1 sampling
- Lattice parameters: a = 4.55 Å and c = 12.92 Å in good agreement with Nagakura et al.[4] having a = 4.553 Å and c = 12.920 Å

Decarburization route

The *decarburization* route (route 5) describes the carbon removal from the Ni carbide which initiated at the top carbide layer and propagated down into the lower layers shown in Figure 4(b). The initial structure for this decarburization route is the Ni covered by its carbide outer layer, which is the same as the final stage of the carburization process (model b3 Figure 4 (b)). During the decarburization process, only the carbide portion is modeled for the process excluding the inner core of Ni shown in model b3 of Figure 4(b). As a result, the first structure for this deoxygenation route is represented by a slab exposing the Ni₃C(001) facet, where the bottom layer of the slab model is fixed to the lattice parameter of the bulk Ni₃C, while for the intermediate models, the top and bottom layers are Ni(111) and Ni₃C(001), respectively. During the coptimization, the bottom Ni and C layers are fixed while the rest of the atoms are relaxed, and the cell shape and size are also allowed to change. The optimized structures are shown in Figure 6.

Similar to the carburization route, this route starts from the pure Ni₃C(001) slab model with 7 Ni-C layers, Figure S4. The slabs labeled 8, 9, 10, 11, 12 and 13 in Fig. S4 have the bottom 2 layers (Ni and O layers) fixed to the lattice parameter of the optimized Ni₃C bulk to imitate the coke removal process, in which the oxidizer reacts with the carbide transforming it into the metallic surface with the Ni₃C core. In addition, the step-wise removal of the carbon is carried out from the top surface down with the same procedure using ISIF $2 \rightarrow 4 \rightarrow 3$.



(atomic color label: grey = Nickel, brown = Carbon)

Figure S4 the unit cell of systems in the *decarburization route*, where the formula is (8) = Ni₈₄C₂₄ // (9) = Ni₈₄C₂₀ // (10) = Ni₈₄C₁₆ // (11) = Ni₈₄C₁₂ // (12) = Ni₈₄C₈ // (13) = Ni₈₄C₄ // (0) = Ni₈₄.

Computational details for the decarburization route

- Number of layers in the slab model = $7 \text{ Ni}_3\text{C}$ layers
- \circ ENCUT = 450 eV
- KPOINTS = Monkhorst-Pack [3] grid of 4x4x1 sampling
- Lattice parameters: a = 4.55 Å and c = 12.92 Å in good agreement with Nagakura et al.[4] having a = 4.553 Å and c = 12.920 Å

B. Reaction coordinate, bond length and configurations of the initial state (IS), transition state

(TS) and final state (FS)



Figure S5.1 reaction coordinate, initial state, transition state and final state: IS, TS, and FS of CH_4 dissociation reaction on Ni(111)



Figure S5.2 reaction coordinate, IS, TS, and FS of H₂ formation reaction on Ni(111)



Figure S5.3 reaction coordinate, IS, TS, and FS of CH* dissociation reaction on Ni(111)



Figure S5.4 reaction coordinate, IS, TS, and FS of CO* formation reaction on Ni(111)



Figure S5.5 reaction coordinate, IS, TS, and FS of C-C formation reaction on Ni(111)

2. Ni(100)



Figure S6.1 reaction coordinate, IS, TS, and FS of C-C formation reaction on Ni(100)

3. Ni3C(001)



Figure S7.1 reaction coordinate, IS, TS, and FS of H₂ formation reaction on Ni₃C(001)



Figure S7.2 reaction coordinate, IS, TS, and FS of CH4 dissociation reaction on Ni₃C(001)



Figure S7.3 reaction coordinate, IS, TS, and FS of C-C formation reaction on Ni₃C(001)



Figure S8.1 reaction coordinate, IS, TS, and FS of H₂ formation reaction on NiO(111)-p(2x2)



Figure S8.2 reaction coordinate, IS, TS, and FS of CH₄ dissociation reaction on NiO(111)-p(2x2)



Figure S8.3 reaction coordinate, IS, TS, and FS of CH* dissociation on NiO(111)-p(2x2)



Figure S9.1 reaction coordinate, IS, TS, and FS of CH₄ dissociation on NiO(100)



Figure S9.1 reaction coordinate, IS, TS, and FS of CH* dissociation on NiO(100)



Figure S9.1 reaction coordinate, IS, TS, and FS of C-C formation on NiO(100)

Table S1 Activation energy for each elementary step							
		Ni(111)	Ni ₃ C(001)	NiO(111)- <i>p</i> (2x2)	Ni(100)	Ni(211)	NiO(100)
set	reaction	E _a (eV)					
Y	$CH_{4(g)} + 2^* \leftrightarrow CH_3^* + H^*$	0.89	0.71	0.91	0.80	0.62	1.86
Y	$\mathrm{H}^{\pmb{*}} + \mathrm{H}^{\pmb{*}} \leftrightarrow \mathrm{H}_{2(g)} + 2^{\pmb{*}}$	0.92	1.00	1.65	0.81	0.77	*N/D
X1	$\mathrm{CH}^{\pmb{*}}+\pmb{*}\leftrightarrow\mathrm{C}^{\pmb{*}}+\mathrm{H}^{\pmb{*}}$	1.38	1.14	1.47	0.52	0.68	2.66
X1	$\mathrm{CO}^{*} + * \leftrightarrow \mathrm{C}^{*} + \mathrm{O}^{*}$	3.43	2.92	*N/D	1.80	1.95	*N/D
X2	$\mathrm{C}^{*} + \mathrm{H}^{*} \leftrightarrow \mathrm{C}\mathrm{H}^{*} + {}^{*}$	0.76	1.02	1.4	0.74	0.92	1.06
X2	$\mathrm{C}^{*} + \mathrm{O}^{*} \leftrightarrow \mathrm{CO}^{*} + {}^{*}$	1.23	2.25	*N/D	2.16	1.74	*N/D
-	$C^{*} + C^{*} = C - C^{*} + *$	0.00	0.10	*N/D	4.0	*N/D	1.3
-	$C-C^* + * = C^* + C^*$	1.7	0.38	*N/D	2.4	*N/D	1.6

C. Activation energies, source of data and the calculated reactivity and stability ratings (RT-R and RT-S)

Table S2 Sources of data for each elementary step

		Ni(111)	Ni ₃ C(001)	NiO(111)- <i>p</i> (2x2)	Ni(100)	Ni(211)	NiO(100)
set	reaction	Sources of data					
Y	$CH_{4(g)} + 2^* \leftrightarrow CH_3^* + H^*$	cNEB	cNEB	cNEB	#ref	#ref	cNEB
Y	$H^* + H^* \leftrightarrow H_{2(g)} + 2^*$	#ref	cNEB	cNEB	#ref	#ref	N/D
X1	$\mathrm{CH}^{\pmb{*}}+\pmb{*}\leftrightarrow\mathrm{C}^{\pmb{*}}+\mathrm{H}^{\pmb{*}}$	cNEB	#Ref	cNEB	#ref	#ref	cNEB
X1	$\mathrm{CO}^{*} + * \leftrightarrow \mathrm{C}^{*} + \mathrm{O}^{*}$	cNEB	#ref	N/D	#ref	#ref	N/D
X2	$\mathrm{C}^{*} + \mathrm{H}^{*} \leftrightarrow \mathrm{C}\mathrm{H}^{*} + {}^{*}$	cNEB	#ref	cNEB	#ref	#ref	cNEB
X2	$\mathrm{C}^{*} + \mathrm{O}^{*} \leftrightarrow \mathrm{CO}^{*} + ^{*}$	cNEB	#ref	N/D	#ref	#ref	N/D
-	$C^{*} + C^{*} = C - C^{*} + *$	cNEB	cNEB	N/D	cNEB	N/D	cNEB
-	C-C* + * = C* + C*	cNEB	cNEB	N/D	cNEB	N/D	cNEB

N/D : not determined

#ref : From Fan et al., Ind Eng Chem Res, 54 (2015) 5901-5913.

cNEB: calculated in this work

			1130(001)	$10(11)-p(2x^2)$	141(100)	1(211)	NIO(100)
set	reaction	RT (%RT)					
Y	$\mathrm{CH}_{4(g)} + 2^{ \ast} \leftrightarrow \mathrm{CH}_{3}^{ \ast} + \mathrm{H}^{ \ast}$	100	113	100	107	119	37
Y	$\mathrm{H}^{*} + \mathrm{H}^{*} \leftrightarrow \mathrm{H}_{2(g)} + 2^{*}$	100	95	51	107	110	*N/D
X1	$\mathrm{CH}^{\pmb{*}}+\pmb{*}\leftrightarrow\mathrm{C}^{\pmb{*}}+\mathrm{H}^{\pmb{*}}$	100	87	110	46	57	*N/D
X1	$\mathrm{CO}^{*} + * \leftrightarrow \mathrm{C}^{*} + \mathrm{O}^{*}$	100	99	*N/D	24	34	189
X2	$\mathrm{C}^{*} + \mathrm{H}^{*} \leftrightarrow \mathrm{C}\mathrm{H}^{*} + ^{*}$	100	86	61	105	93	*N/D
X2	$\mathrm{C}^{*} + \mathrm{O}^{*} \leftrightarrow \mathrm{CO}^{*} + {}^{*}$	100	56	*N/D	62	90	83
	average RT-S	100	82	86	59	68	136
	average RT-R	100	104	76	114	107	37

Table S3 Stability ratings (RT-S) and Reactivity ratings (RT-R) and their average values for each elementary step | Ni(111) Ni₃C(001) NiO(111)-p(2x2) Ni(100) Ni(211) NiO(100)

D. Calculation of ZPE, U and S correction

From transition state theory (TST), the rate constant is written as

$$k_i = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{k_B T}}$$

From the equation, $\Delta G^{\ddagger,\circ}$ is the change of standard molar Gibbs free energy between the transition state (TS) and the initial state (IS) or the reactant, where it is represented as

$$\Delta G^{\ddagger,\circ} = \Delta E_{DFT} + \Delta E_{ZPE} + \Delta U^{\circ} - T\Delta S^{\circ}$$

- ΔE_{DFT} is the activation energy of the desired elementary step obtained directly from the DFT calculation.
- ΔE_{ZPE} is the zero-point energy calculated by the

$$\Delta E^{ZPE} = \sum \frac{hv_i}{2}$$

the v_i = vibrational frequency obtained via the vibrational frequency calculation h = Planck's constant

- ΔU° = standard molar internal energy which includes standard molar vibrational, translational and rotational internal energies
- ΔS° = standard molar entropy which includes standard molar vibrational, translational and rotational entropies

The equation for the calculation of the standard molar translational, rotational and vibrational internal energies and entropy can be found in [5-7]. The calculated ZPE, U and S values for all of the elementary steps are shown in Table S4 below.

Table S4 Zero-point energy, entropy and internal energy corrections for every DRR elementary step on Ni(111) at temperature = 1000 K and CO_2/CH_4 ratio = 1

Elementary step	reaction	E _a (eV)	$\Delta ZPE (eV)$	$\Delta U (eV)$	$T\Delta S (eV)$	$\Delta G (eV)$
1	$CH4(g)+2*\leftrightarrow CH3*+H*$	0.89	-0.04	0.20	-1.29	2.34
2	$\mathrm{CH3}^{*+*}{\leftrightarrow}\mathrm{CH2}^{*+}\mathrm{H}^{*}$	0.70	-0.13	-0.01	-0.03	0.59
3	$CH2^{*+*} {\leftrightarrow} CH^{*+}H^{*}$	0.35	-0.12	-0.02	0.04	0.17
4	$\mathrm{CH}^{*+*} {\leftrightarrow} \mathrm{C}^{*+} \mathrm{H}^{*}$	1.33	-0.17	-0.01	-0.02	1.17
5	$CO2(g)+2*\leftrightarrow CO*+O*$	0.67	-0.04	0.17	-1.44	0.62
6	$C^{*}\!\!+\!\!O^{*}\!\!\leftrightarrow\!\!CO^{*}\!\!+\!\!*$	1.59	-0.04	-0.05	-0.09	1.59
-1	$CH3*+H*\leftrightarrow CH4(g)+2*$	0.90	0.01	-0.05	-0.04	0.90
-2	CH2*+H*↔CH3*+*	0.63	-0.02	-0.03	0.03	0.55
-3	CH*+H*↔CH2*+*	0.69	-0.07	-0.02	0.12	0.48
-4	$C^{*}\!\!+\!\!H^{*}\!\!\leftrightarrow\!\!CH^{*}\!\!+\!\!*$	0.81	-0.10	-0.01	0.03	0.67
-5	$CO*+O*\leftrightarrow CO2(g)+2*$	1.65	0.02	-0.01	-0.03	1.69
-6	$CO^{*+*}\leftrightarrow C^{*+}O^{*}$	2.94	-0.05	-0.06	-0.26	3.09

 E_a = activation energy obtained directly from cNEB calculation without any ZPE, U and S corrections

 $\Delta ZPE =$ zero-point energy change from the initial state (IS) to the transition state (TS)

 ΔU = internal energy change from the initial state (IS) to the transition state (TS)

 ΔS = entropy change from the initial state (IS) to the transition state (TS)

 ΔS = Gibbs free energy change from the initial state (IS) to the transition state (TS)

E. Construction of the ratings concept

The ratings concept was introduced as a screening tool for estimating reactive and stable DRR catalysts based on the comparison of catalysts performance[8].

Briefly, the comparison of the DRR catalyst performances via the ratings concept can be explained via the setup of a thermometer scale. Similarly to the thermometer scale, the setup of our ratings concept has (1) the performance of the DRR catalysts as a parameter to be compared (equivalent to temperature), (2) the scale called "the ratings scale" that reads the performance of the DRR catalysts in units of percent rating (%RT) with a constant step size, where the value of step size is tested and selected to be 0.015 eV energy change per 1 percent rating[8, 9] and (3) one reference point which is the performance of the reference catalysts set to 100 %RT to which other catalysts are benchmarked. In this way, the catalysts with ratings above 100 are considered to have higher performance than the reference catalyst.

However, the description of the performance should not only include reactivity but also stability. This is because coking is one of the main factors affecting the DRR performance. Thus, the rating concept determines how reactive and stable the catalyst should be in order to achieve a high rate of reaction while suppressing coke formation via two parameters: reactivity rating (RT-R) and stability rating (RT-S) derived from the following procedure.

- 1. Select the reference catalyst which will be the benchmark for others to compare with. In our work, the Ni(111) surface was selected and represented by the slab model.
- 2. Designate the reactivity (set Y) and stability (X1 and X2) sets having activation energies of specific elementary steps accounting for reactivity and stability of the catalyst of interest as follows:
 - 2.1. Set X1, the coke removal reaction set integrated by the activation energies of:
 - 2.1.1. reverse elementary step 4 (C* + H* \rightarrow CH* + *)
 - 2.1.2. forward elementary step 6 (C* + O* \rightarrow CO* + *)
 - 2.2. Set X2, the coke formation reaction set integrated by the activation energies of:
 - 2.2.1. forward elementary step 4 (CH* + * \rightarrow C* + H*)
 - 2.2.2. reverse elementary step 6 (CO* + * \rightarrow C* + O*)
 - 2.3. Set Y, the reactivity set integrated by the activation energies of:
 - 2.3.1. forward elementary step 1 ($CH_{4(g)} + 2^* \rightarrow CH_3^* + H^*$)
 - 2.3.2. forward elementary step 5 ($CO_{2(g)} + 2^* \rightarrow CO^* + O^*$)
 - 2.3.3. forward elementary step 7 (H* + H* \rightarrow H_{2(g)} + 2*)
- 3. Rate each set of the selected catalysts with respect to the reference catalyst via either the direct or reverse rating scale calculated via the following equations.

direct rating scale (for set X2):
$$\frac{E_a - E_{a,0}}{RT - RT_0} = +|\Phi|$$
 Equation 1

reverse rating scale (for sets X1 and Y):
$$\frac{E_a - E_{a,0}}{RT - RT_0} = -|\Phi|$$
 Equation 2

* Φ is the Rating scale ratio which is the step size of the rating scale which is set to 0.015eV/1%RT

For set X1 (coke removal) and Y (reactivity), the lower the E_a for these sets the easier for the system to remove coke and activate reactants, while for set X2 (coke formation), the higher the E_a the more difficult for the system to form coke. As a result, higher reactivity rating (RT-R) would result from lower E_a of set Y (reactivity), while higher stability rating (RT-S) came from lower E_a of set X1 (coke removal) yet higher E_a of set X2 (coke formation). Hence, the direct rating scale is used on set X2, while the reverse rating scale is used on set X1 and Y. Then, the rating (RT) of the selected catalyst is determined. (RT of the reference system are assigned to be 100 %)

4. Calculate the average reactivity rating (RT- R_{avg}) from the arithmetic mean of stability rating in set Y and for average stability ratings (RT- S_{avg}), stability ratings in set X1 U X2 are averaged as the following equations:

$$RT - R_{avg} = \frac{1}{n} \sum_{i=1}^{n} RT - R_i$$
$$RT - S_{avg} = \frac{1}{m} \sum_{i=1}^{m} RT - S_i$$

Equation 3

Equation 4

n = number of all elementary reactions in set Y m = number of all elementary reactions in set X1 U X2



Figure S10 (a) reactivity surface (RS), (b) stability surface (SS) as total rate of coke formation and (c) stability surface (SS) as total rate of coke removal (reaction condition at T = 1000 K, $P_{CH4} = P_{CO2} = 1$ bar, $P_{H2} = P_{CO} = 0.1$ bar)

- 5. Construct the reactivity surface (RS) and stability surface (SS) shown in Figure S10, where the reactivity surface (RS) is the plot of rate of total rate of DRR as a function of RT-R_{avg} and RT-S_{avg}, while the stability surfaces (SS) are the plots of rate of coke formation and coke removal both as functions of RT-R_{avg} and RT-S_{avg}. Additionally, Figure S10(b) depicts the total coke formation while Figure S10(c) illustrates the total coke removal.
- 6. Plot x and y coordinate of the selected catalysts onto RS and SS as $x = RT-S_{avg}$ and $y = RT-R_{avg}$. Note that for both RS and SS, the RT-S_{avg} and RT-R_{avg} of the reference catalyst is set to 100 %RT as described previously.
- 7. Analyze the reactivity surface (RS) for the rate of reaction and screen for reactive catalysts, where a high rate of reaction means high reactivity.
- 8. Analyze the stability surfaces (SS) and locate if the selected catalyst is coke-resistant or not. For the stable catalyst criteria, the catalyst should exhibit higher coke removal than formation where the deciding parameter is the difference between the total rate of coke formation and removal of each catalyst.

F. Calculation of coking zone and coke formation/removal boundary

The coke boundary is calculated from two equations which give the contour plot of coke formation zone and coke removal zone, respectively for all indexes of (RT-S, RT-R).

- Equation 1: the coke formation zone = (total rate of all C forming elementary reactions) (total rate of all C removing elementary reactions)
- Equation 2: the coke removal zone = (total rate of all C removing elementary reactions) (total rate of all C forming elementary reactions)

With respect to the above equation, for the coke formation zone to exist, all the coke forming reaction rates must be higher than all the coke removing reaction rates. If some indexes of (RT-S, RT-R) give negative rate when calculated with equation 1, then that location is considered the coke removal zone. Likewise, when calculating with equation 2, any locations that give positive rate difference will be the coke removal zone and the locations of negative rate difference will be the coke formation, the boundary separating these two zones is named "coking boundary", where the total rate of coke formation is equal to the total rate of coke removal. The construction is shown in Figure S11



Figure S11 Construction of coke formation and removal zones

So, this line is used for the stability screening. When applying this coking boundary line on the DRR rate contour plot, we can screen catalyst's reactivity and stability at the same time, where the good candidates must have high DRR rate and also be in the coke removal zone as shown in Figure S12.



Figure S12 the DRR rate with coking boundary

This figure states that although the high DRR rate is found on the left side of the coking boundary, the left side has low stability since it is the coke formation zone as can be seen from Figure S11(C). Therefore, to arrive at the reactive and stable DRR catalysts, they must locate on the right side of the boundary and at the highest rate of coke removal which is determined from Figure S11(D).

G. Changes in the rate of reaction and coke formation/removal during catalyst evolution

Table 1. Changes in the rate of reaction (TOF_DRR), total coke formation (TOF_C_{gen}) and total coke removal (TOF_C_{rem}) when the catalyst surface evolves at temperature = 1000 K and CO_2/CH_4 feed ratio = 1.0

Bouto*	Log Rate change (%)**					
Koule	TOF_DRR	TOF_C_{gen}	TOF_C_{rem}			
$(1) \operatorname{Ni}(100) \rightarrow \operatorname{NiO}(100)$	-73.6	-122.5	-169.1			
$(1) \operatorname{Ni}(111) \rightarrow \operatorname{NiO}(111) - p(2x2)$	+23.5	+1137.8	-128.8			
$(2) \operatorname{Ni}(111) \rightarrow \operatorname{Ni}_{3}C(001)$	+28.3	+1368.5	+21.8			
(3) Ni ₃ C(001) \rightarrow NiO(111)-p(2x2)	-3.7	-18.2	-123.7			
$(4) \operatorname{NiO}(100) \rightarrow \operatorname{Ni}(100)$	+278.5	+544.7	+244.7			
$(4) \operatorname{NiO}(111) \text{-p}(2x2) \rightarrow \operatorname{Ni}(111)$	-19.1	-109.6	+446.8			
(5) $Ni_3C(001) \rightarrow Ni(111)$	-22.0	-107.9	-17.9			
(6) NiO(111)-p(2x2) \rightarrow Ni ₃ C(001)	+3.8	+22.2	+522.3			

* Route number in parenthesis (#) refers directly to the Surface transformation network in Figure 1 (surface1 \rightarrow surface2 refers to the surface transformation route that starts with surface1 and ends as surface2 when the surface transformation process is complete)

** The calculation of Log Rate change uses the rate from Table 5 using the simple percentage changes as: Log Rate change_{surfl→surf2} (%) = (Log Rate_{surface,2}- Log Rate_{surface,1})/ Rate_{surface,1}, where positive (+) and negative (-) signs mean rate increase and decrease, respectively.

In the following section, we analyzed how the reactivity and stability in terms of DRR, coke formation and coke removal rates changed as a result of surface transformations as illustrated in Figure 1. For the fresh Ni catalyst, the surface was modeled as the metallic surface of Ni [10]. At the initial stage of the reaction, the surface would transform via either oxidation or carburization depending on the adsorbates. When the oxide and carbide surfaces form as a result of these processes, they could transform back to the metallic Ni via deoxygenation and decarburization, respectively. According to this, the effects of oxidation, deoxygenation, carburization, and decarburization routes on catalyst performance were discussed as follows.

• Transformation route 1&4: oxidation-deoxygenation

The oxidation route of the metallic Ni surface to form Ni oxide labeled as route 1 in Figure 1 occurs during the reaction between the metallic surface and oxygen atoms that are generated from the dissociation of CO_2 reactant [11]. This route is modelled on two different facets: the (100) facet which describes the transformation of Ni(100) to NiO(100), and the (111) facet illustrating

the Ni(111) facet transforming to NiO(111). that finally undergoes octopolar surface reconstruction and forms the NiO(111)-p(2x2)[12, 13]. Referring to Table 6, it is found that for the oxidation on the (100) facet (Ni(100) \rightarrow NiO(100)), the oxide surface shows lower DRR reactivity than the metallic surface. Regarding coke-resistance, although the log rate of coke removal is low on the oxide, it is higher than the coke formation resulting in a coke-resistant surface. Thus, the oxidation on the (100) facet would lower the reactivity but enhance cokeresistance. On the (111) facet, the Ni(111) \rightarrow NiO(111)-p(2x2) route, although the reactivity would slightly increase, the system is not coke-resistant due to the increase in coke formation and decrease in coke removal. It can be clearly seen that if the oxidation of the Ni catalyst takes place on the (100) facet, the resulting oxide surface would be less reactive but still coke-resistant, while on the (111) facet, the catalyst surface would be more reactive but unfortunately more prone to coke deposition. In summary, for the oxidation route 1, the degree of reduction on the catalyst from the oxide to the metallic surface obtained in the reduction step of catalyst preparation may affect directly the performance of the catalyst. To emphasize, an incomplete reduction on the (100) facet would lead to a surface with a high amount of NiO(100) compared to Ni(100) making the characteristics of the catalyst become more oxide-like which has high coke-resistance but would be less reactive. In contrast, if a poor reduction occurs on the (111) facet, the catalyst would be more active but it would not be coke-resistant. Hence, coke-resistant Ni catalysts should have a high degree of oxidation on the (100) facet, but low on the (111) facet.

• Transformation route 2&5: carburization-decarburization

When the DRR begins, the metallic Ni phase can transform to carbide via the carburization denoted as route 2 (Figure 1), by the reaction between the surface and adsorbed carbon atoms formed via CH_4 and CO_2 dissociations[14]. The changes in catalyst performance due to this route are presented in Table 6 and is investigated on the (111) facet. As a result, the models of metallic and carbide surfaces involving in the carburization-decarburization processes are chosen to be Ni(111) and Ni₃C(001) as analogous (111) surfaces[7]. The carbide surface is observed experimentally to have high reactivity but low stability [15, 16]. This characteristic is obvious from Table 6 because when the Ni(111) surface transforms into the Ni₃C(001) the rate of DRR reaction rises along with a decrease in the stability due to a great increase in coke formation from log rate of -0.20 to 2.5. Although the coke removal rate did increase, its value of 1.7 is lower than

that of coke formation resulting in more coke formation than removal, thus, it is not coke-resistant. In conclusion, the formation of the carbide would enhance the catalyst's reactivity but lower the coke-resistance by promoting high-order coke formation.

• Transformation route 3&6: oxide to carbide & carbide to oxide

Route 3 represents the situation where the carbide transforms to the oxide surface. Evidence supporting such route has been observed by Yuan et al.[17], where the $CO_2(g)$ reactant could react and eliminate the Ni carbide portion on the sample. This was confirmed by an absence of the Ni_xC peak at 283.6 eV measured by a Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). Furthermore, the excess oxygen atoms produced from CO_2 can initiate the oxidation of the surface resulting in the formation of the oxide surface. Note that this event could be considered if the metallic surface is formed via the elimination of carbide but instantly oxidized as soon as the metallic phase forms. To model this event, let us consider the (111) facet, where the Ni₃C(001) and NiO(111)-p(2x2) are chosen as the starting and final structures of this route, respectively since both (111) surfaces are structurally analogous to the Ni(111).

On the other hand, the route 6 represents the transformation of oxide to carbide which was demonstrated by Cocke et al.[11] In this case, the decomposition of the Ni oxide under the presence of adsorbed carbon atoms on the surface can lead to the formation of Ni carbide. As a result, referring to Table 5, if the surface transforms from oxide to carbide, it would be more DRR reactive but less coke-resistant since the coke formation rises while the coke removal falls. This again confirms the high reactivity but low coke-resistance of the carbide and the high stability but low reactivity of the oxide.

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