# **Supporting Information**

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## 1. Catalyst support descriptor (CSD) theoretical description

## Resonance interactions between oxides and d-states of nanocluster

Resonance contribution to the Hamiltonian of the d-states of a nanocluster can be expressed previously:<sup>1</sup>

$$H_{\mu\nu}^{res} = \sum_{i,j} \beta_{\mu i} \beta_{\nu j} \sum_{n,k} \frac{\langle i \mid nk \rangle \langle nk \mid j \rangle}{E_d - E_{nk}}$$
 Equation S1

where indices  $\mu$  and  $\nu$  correspond to the d-states, i and j enumerate atomic orbitals of the support, summation over n, k goes over band states of the support,  $E_d$  – is energy of the d-states and  $E_{nk}$  – band energy.

Exact calculation of the resonance contributions requires detailed knowledge of the electronic structure of the support and d-states of the nanocluster. However, qualitative analysis of this equation allows to suggest functional form of a descriptor reflecting the magnitude of electron transfer between support and transition metal clusters. To do that we make the following approximations:

1. The most significant contribution to the electron transfer comes from interaction of the d-states with the frontier states of the valence band, which mostly consist of O2p in the case of oxides. It allows to restrict summation over all atomic orbitals of the support to the summation over oxygen 2p orbitals.

2. Density of states of the O2p valence band typically looks like a narrow peak, therefore we use a constant value of energy for all band states  $E_{nk} = E_{2p}$ .

3. Typically, non-diagonal orbital-projected density matrix elements are much smaller compared to the diagonal one, which allows to omit all the terms whith i  $\neq$  j.

4. We assume that all oxygen 2p atomic orbitals are equivalent and have the same coupling with the d-states of the nanocluters (mean field approximation).

These approximations allow to simplify the equation for the resonance contribution:

$$H_{\mu\nu}^{res} \approx \sum_{i} \beta_{\mu i} \beta_{\nu i} \frac{P_{ii}}{E_d - E_{2p}} = const \sum_{i} \frac{1}{E_d - E_{2p}} \qquad Equation S2$$

where the summation now goes over all 2p orbitals of oxygen interacting with the nanocluster. The sum is proportional to the number of these orbitals, hence proportional to the surface density of the base sites. These considerations yield the equation (3) of the manuscript.

# 2. X-ray photoelectron spectroscopy (XPS) measurements

X-ray photoelectron spectroscopy (XPS) measurements were conducted for  $CeO_2$  using Thermo Scientific K-Alpha instrument, with no pre-treatment applied to the samples prior to the measurements. The data were processed with CASAXPS (Version 2.3.17). The data was charge corrected to the reference C 1s signal at 285.0 eV.

The XPS fittings were performed using the following parameters:

- O 1s LA(1.53,243) line shape, Shirley background, full width at half maximum (FWHM) was kept below 3 eV;
- O KLL LA(1.53,243) line shape, linear background, full width at half maximum (FWHM) was kept below 4 eV.
- The O 1s peak signal can be divided in three signals: lattice oxygen atoms with a binding energy generally in the range of 529–530 eV (1); then a second peak between 530-532 eV (2) assigned as hydroxide and then 532-533 eV (3) to carbonate species.<sup>2</sup> Therefore, we constrain the position of the peak (2) to be between 1-2 eV from peak (1); and peak (3) to be 2-3 eV from peak (1). For the O KLL, same approach was used with a constrain of the position of peak (2) to be 2-3 eV from peak (3) to be 3-4 eV from peak (1). In a few instances, a peak at a higher binding energy than 533 eV appears, which some reports attribute to adsorbed water. However, as this remains a topic of ongoing debate, it is not addressed in this work, as it falls outside the scope of our focus.

#### CeO<sub>2</sub> support XPS measurements



**Figure S1**. X-ray photoelectron spectroscopy (XPS) measurements for  $CeO_2$  were analysed before **a-b**) and after **c-d**)  $CeO_2$  surface argon sputtering. O 1s and O KLL spectra after argon sputtering show results very similar to those before argon sputtering, with a slight increase on oxygen lattice signal as expected for  $CeO_2$ .



**Figure S2**. X-ray photoelectron spectroscopy (XPS) measurements for  $CeO_2$  to observe the effect of surface argon sputtering over time for **a-c**) C 1s, O 1s, and O KLL. The aim of these measurements was to confirm the assignment of lattice oxygen, hydroxide and carbonate species, as the surface argon sputtering process should completely or partially remove hydroxide and carbonate species, resulting in a decrease of these two species after argon sputtering and an increase in the lattice oxygen signal. The bottom measurement of each figure shows the spectra before argon sputtering, used as a reference. It is important to highlight that in the case of  $CeO_2$ , lattice oxygen is the predominant component even without argon sputtering, so no major changes were expected. After the first argon sputtering cycle, a slight decrease in the signal of the peak at the higher binding energy component is observed for the O 1s spectra. This indicates that the signal of the peak associated with hydroxide and carbonate species is slightly lower after the initial argon sputtering, which is also observed in the O KLL spectra.

#### La2O3 support XPS measurements



**Figure S3**. X-ray photoelectron spectroscopy (XPS) measurements for  $La_2O_3$  were analysed before **a**-**b**) and after **c**-**d**)  $La_2O_3$  surface argon sputtering. Before argon sputtering, the O 1s and O KLL spectra indicated that carbonate was the major component. However, after sputtering, the spectra revealed that lattice oxygen became the primary component, with a minor formation of hydroxide species on the  $La_2O_3$  surface. The peak at low kinetic energy, located near the carbonate species, leads to an overestimation of the lattice oxygen concentration in the O KLL spectra. However, it does not affect the peak position of lattice oxygen, as demonstrated after argon sputtering, where lattice oxygen became the major component. The low kinetic energy peak, which is characteristic of  $La_2O_3^3$ , lies outside the scope of this study, and its nature is therefore not discussed in detail.



**Figure S5**. X-ray photoelectron spectroscopy (XPS) measurements for  $La_2O_3$  to observe the effect of surface argon sputtering over time for **a-c**) C 1s, O 1s, and O KLL. The aim of these measurements was to confirm the assignment of lattice oxygen, hydroxide and carbonate species, as the surface argon sputtering process should completely or partially remove hydroxide and carbonate species, resulting in a decrease of these two species after argon sputtering and an increase in the lattice oxygen signal. The bottom measurement of each figure shows the spectra before argon sputtering, used as a reference. A significant change in the height of the major peaks between the lower and higher binding energy components is observed for the O 1s spectrum after the first argon sputtering cycle. This indicates that lattice oxygen becomes the major component following the initial argon sputtering cycle. This behaviour is also observed in the O KLL spectrum.

#### Y<sub>2</sub>O<sub>3</sub> support XPS measurements



**Figure S6**. X-ray photoelectron spectroscopy (XPS) measurements for  $Y_2O_3$  were analysed before **a-b**) and after **c-d**)  $Y_2O_3$  surface argon sputtering. Before argon sputtering, the O 1s and O KLL spectra indicated that carbonate was the major component. However, after sputtering, the spectra revealed that lattice oxygen became the primary component.



**Figure S7**. X-ray photoelectron spectroscopy (XPS) measurements for  $Y_2O_3$  to observe the effect of surface argon sputtering over time for **a-c**) C 1s, O 1s, and O KLL. The aim of these measurements was to confirm the assignment of lattice oxygen, hydroxide and carbonate species, as the surface argon sputtering process should completely or partially remove hydroxide and carbonate species, resulting in a decrease of these two species after argon sputtering and an increase in the lattice oxygen signal. The bottom measurement of each figure shows the spectra before argon sputtering, used as a reference. A significant change in the height of the major peaks between the lower and higher binding energy components is observed for the O 1s spectrum after the first argon sputtering cycle. This indicates that lattice oxygen becomes the major component following the initial argon sputtering cycle. This behaviour is also observed in the O KLL spectrum.

#### MgO support XPS measurements



**Figure S8**. X-ray photoelectron spectroscopy (XPS) measurements for MgO were analysed before **a-b**) and after **c-d**) MgO surface argon sputtering. Before argon sputtering, the O 1s and O KLL spectra indicated that hydroxide species were the major component. However, after sputtering, the spectra revealed that lattice oxygen became the primary component.



**Figure S9**. X-ray photoelectron spectroscopy (XPS) measurements for MgO to observe the effect of surface argon sputtering over time for **a-c**) C 1s, O 1s, and O KLL. The aim of these measurements was to confirm the assignment of lattice oxygen, hydroxide and carbonate species, as the surface argon sputtering process should completely or partially remove hydroxide and carbonate species, resulting in a decrease of these two species after argon sputtering and an increase in the lattice oxygen signal. The bottom measurement of each figure shows the spectra before argon sputtering, used as a reference. A significant shift to lower binding energy for the C 1s and O 1s spectra, and higher kinetic energy for the O KLL spectra, is observed after the first argon sputtering cycle. This shift suggests a decrease in the content of hydroxide species and an increase in the signal for lattice oxygen.

CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and MgO supports XPS measurements



**Figure S10**. X-ray photoelectron spectroscopy (XPS) measurements of **a-d**) Ce 3d, La 3d, Y 3d and Mg 1s, respectively.

## Sc<sub>2</sub>O<sub>3</sub> support XPS measurements



**Figure S11**. **a-b**) C 1s and Sc 2p spectra for  $Sc_2O_3$ . **c-d**) The O 1s and O KLL spectra both show lattice oxygen as the major component, similar to what is observed in CeO<sub>2</sub>.

Table S1.         Summary of the XPS binding energy and kinetic energy values for the O 1s and O KLL spectra,
respectively. The values were averaged from measurements taken at three different locations using
Thermo Fisher K-Alpha measurements conducted before argon sputtering.

		O 1s (eV)			O KL <sub>23</sub> L <sub>23</sub> (eV)	
Supports	Lattice	Hydroxida	Carbonate	Carbonate	Hydrovide	Lattice
	oxygen	Hydroxide	species	species	Hydroxide	oxygen
CeO <sub>2</sub>	529.4 ± 0.1	531.2 ± 0.1	532.4 ± 0.3	509.5 ± 0.3	511.0 ± 0.2	513.4 ± 0.1
$La_2O_3$	529.0 ± 0.1		531.5 ± 0.3	509.8 ± 0.3	-	513.4 ± 0.1
$Y_2O_3$	529.4 ± 0.1		531.8 ± 0.2	509.2 ± 0.1	-	512.2 ± 0.2
Sc <sub>2</sub> O <sub>3</sub>	530.0 ± 0.1	531.4 ± 0.1	532.9 ± 0.2	507.3 ± 0.2	509.3 ± 0.2	511.3 ± 0.1
MgO	529.6 ± 0.1	531.6 ± 0.1	-	-	$508.1 \pm 0.1$	510.2 ± 0.1

## 3. Thermal programmed desorption (TPD) of CO<sub>2</sub>

$$d = \frac{6000}{\rho_{He} \cdot A_{BET}}$$

Table S2. Metal oxides A	A <sub>BET</sub> surface area	for CO <sub>2</sub> desorption	measurements.
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Entry	Support	Sample mass (mg)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Basic sites no reduction (μmol m <sup>-2</sup> )	Basic sites reduction (μmol m <sup>-2</sup> )
1	Y <sub>2</sub> O <sub>3</sub>	23	15.7	3.3	3.3
2	$La_2O_3$	30	13.7	2.0	1.8
3	CeO <sub>2</sub>	15	77.7	0.3	1.7
4	$Sc_2O_3$	48	6.7	1.1	1.4
5	MgO	40	116.3	0.4	0.7



**Figure S12.**  $CO_2$  desorption from metal oxide supports after baseline correction: (a) data without normalisation to the support surface area and (b) data normalised to the support surface area, used to calculate CSD values.

The concentrations of Lewis base site (LBS) were measured under two conditions: with and without  $H_2$  reduction prior  $CO_2$  desorption experiments for all samples (see results in Table S2).  $CeO_2$  was the only metal oxide that exhibited significant changes, while no notable changes were observed for the other metal oxides (Table S2). This behaviour is attributed to  $CeO_2$ 's high reducibility under hydrogen and/or vacuum environments.<sup>4</sup> Since the Ru atoms were deposited under vacuum conditions (with a background pressure of  $3 \times 10^{-8}$  torr and working pressure under argon of  $3 \times 10^{-3}$  torr), the metal atoms landed on a highly reduced metal oxide surface. Therefore, we used the  $CO_2$  TPD results with prior  $H_2$  reduction to mimic the vacuum conditions of the Ru nanoclusters formation. This approach showed very good agreement with our catalysis findings.

# 4. Ammonia synthesis

Table S3. Catalyst and support masses for c	atalytic testing. All catalytic materials	were furthermore
diluted in 2.3 g of SiC.		

Entry	Catalyst	Support	Mass	Volume	Added	Added	Ru
		density	support	Ru on	support	support	/mg
		(g/L)	with Ru /	support /	mass /	V / mL	
			mg	mL	mg		
1	Ru/CeO <sub>2</sub>	65	115	1.700	0	0	1.7
2	$Ru/Y_2O_3$	543	223	0.412	591	1.09	1.7
3	Ru/MgO	170	100	0.590	195	1.03	1.7
4	$Ru/La_2O_3$	77	85	1.104	39	0.51	1.7
5	$Ru/Sc_2O_3$	650	196	0.300	910	1.40	1.7



Figure S13. Productivities of Ru onto Sc<sub>2</sub>O<sub>3</sub>, MgO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> for 58 h on stream.



**Figure S14.** (a) Effect of hydrogen on  $Ru@Sc_2O_3$  not presented catalysts in the main paper, b-d)  $N_2$  order for the not presented catalysts in the main paper.



Figure S15. Arrhenius Plot for Ru/CeO<sub>2</sub>, Ru/Y<sub>2</sub>O<sub>3</sub>, Ru/Sc<sub>2</sub>O<sub>3</sub>, Ru/La<sub>2</sub>O<sub>3</sub> and Ru/MgO.

## N\* binding strength

For TPD analysis, methods developed elsewhere were used.<sup>5</sup> In short, the coverage of N\* was assumed to be 1 and the system is considered to reach equilibrium. In accordance with previous reports, the pre-exponential factor A was assumed to be  $1.5 \cdot 10^{15} \text{ s}^{-1.6}$ 

For TPA analysis, the rate constant for adsorption  $(k_{ads})$  the following rate law was assumed:

$$r = k_{ads} P_{N2} \theta_*^2$$

Under initial conditions, where the desorption of  $N_2$  from the surface can be neglected,  $\theta_*$  can be calculated as:

$$\theta_* = \theta_{tot} - \theta_{N*}$$

Hereby  $\theta_{N*}$  can be calculated from the amount of N<sub>2</sub> adsorbed onto the Ru surface.

The equilibrium constant for nitrogen adsorption can thus be calculated for varying temperatures because by definition:

$$K_{eq}(T) = \frac{k_{ads}(T)}{k_{des}(T)}$$

Using values of  $K_{eq}$ ,  $\Delta H$  and  $\Delta S$  can be derived from the Van't Hoff equation.

## Additional discussion:

Traditionally N\* binding strength is used as a descriptor to predict the catalytic activity of a surface in ammonia synthesis.<sup>7-9</sup> Experimentally the N\* binding strength can be determined by temperature programmed adsorption (TPA), temperature programmed desorption (TPD) and  ${}^{15}N_2$ : ${}^{14}N_2$  scrambling experiments.<sup>6, 10-14</sup> Hereby TPA experiments measure the rate constant for dissociative nitrogen adsorption ( $k_{ads}$ ),<sup>6, 14</sup> whilst from TPD experiments the rate constant for the desorption process can be extracted ( $k_{des}$ ).<sup>5, 6, 10, 15, 16</sup> As by definition the equilibrium constant ( $K_{eq}$ ) is defined by the fraction of the adsorption divided by the desorption rate constant, equilibrium constant can be solved and  $\Delta$ G,  $\Delta$ H and  $\Delta$ S can be obtained for the dissociative nitrogen adsorption.

As  $Y_2O_3$ ,  $CeO_2$  and MgO span the entire width of the catalyst support descriptor (CSD) values determined previously,  $Ru/Y_2O_3$ ,  $Ru/CeO_2$  and Ru/MgO were chosen to determine the nitrogen bonding strengths. In general, the activation energy of adsorption decreases from Ru/MgO to  $Ru/CeO_2$ and  $Ru/Y_2O_3$  whilst the activation energy for the desorption is within the same range for all samples ( $Ru/Y_2O_3$  has a slightly smaller activation energy of desorption). Interestingly, the decrease in the activation energy of dissociative adsorption and the CSD displays a linear correlation. It is important to note that for  $Ru/CeO_2$  and  $Ru/MgO N_2$  TPD experiments were – in contrast to  $Ru@Y_2O_3$  - not successful but instead TPD of spent catalyst after performing ammonia synthesis were analysed. The difference in acquisition method might explain the difference in between the desorption activation energies observed  $Ru/Y_2O_3$  and  $Ru/CeO_2$ , respectively Ru/MgO. Furthermore, the spent catalysts (Ru/MgO and  $Ru/CeO_2$ ) displayed a secondary desorption process at higher temperatures, which was disregarded for this analysis. To analyse the acquired TPD data, we used a published program and thus we had to made an assumption that the coverage of  $N^*$  is assumed to be 1 which in reality is not the case.<sup>5</sup> The obtained values are in general in good agreement with previous reports. <sup>6, 13, 17</sup> For instance, the activation energy of desorption is in the same range as previously reported for Ru/MgO and Ru/C12A7:O<sup>2-</sup> but as expected significantly higher as reported to electride materials.<sup>6, 13, 17</sup> The pre-exponential factor found for the dissociative adsorption of nitrogen is a magnitude higher as reported previously for Ru/MgO, but still represent very low values indicating a highly activated process for the activation of nitrogen.<sup>6</sup> Finally, the activation energies found for the Ru/MgO prepared by wet chemical deposition but fall again in the same range as reported for Ru@C12A7:O<sup>2-,6, 13, 17</sup>

Using the Arrhenius parameters developed in the previous section,  $k_{ads}$  and  $k_{des}$  can be calculated at various temperatures and consequently  $\Delta H$  and  $\Delta S$  (and thus  $\Delta G^0$ ) can be estimated for the dissociative adsorption of N<sub>2</sub> on the investigated catalysts. As expected, by the lowering activation energy found for the adsorption (whilst desorption activation energies remained constant), the  $\Delta H$  decreases from Ru/MgO (-12.3 kJ mol<sup>-1</sup>) over Ru/CeO<sub>2</sub> (-62.7 kJ mol<sup>-1</sup>) to Ru/Y<sub>2</sub>O<sub>3</sub> (-82.8 kJ mol<sup>-1</sup>), indicating a stronger heat of adsorption in the order. This finding is also reflected in the calculated  $\Delta G^0$  values, reflective of a stronger binding strength. Compared to reported values, these values are lower as reported for Ru/MgO prepared by wet chemical methods.<sup>6</sup> For instance,  $\Delta H$  has been reported to be -97.4 kJ mol<sup>-1</sup>, whilst the values found here range from -12.3 kJ mol<sup>-1</sup> to -82.8 kJ mol<sup>-1</sup>, thus  $\Delta G^0$  values determined for our catalysts are in 10 kJ mol<sup>-1</sup> to 15 kJ mol<sup>-1</sup> higher.<sup>6</sup> The difference between the determined values in this work are most likely to be associated with the methodology used to determine the Arrhenius parameters of the desorption process (as mentioned earlier a coverage of 1 is assumed).<sup>5, 6</sup> It is important to note that the  $\Delta H$  values found here are in the same range found previously for Ru/C12A7:O<sup>2-,17</sup>



**Figure S16.** Temperature programmed adsorption of  $N_2$  on for (a)  $Ru/Y_2O_3$ , (b)  $Ru/CeO_2$  and (c) Ru/MgO. Arrhenius plots for (a)  $Ru/Y_2O_3$ , (e)  $Ru/CeO_2$  and (c) Ru/MgO.



**Figure S17.** Temperature programmed desorption of  $N_2$  on for (a)  $Ru/Y_2O_3$ , (b)  $Ru/CeO_2$  and (c) Ru@MgO. Comparison with simulated desorption TPD spectra (red) for (a)  $Ru/Y_2O_3$ , (e)  $Ru/CeO_2$  and (c) Ru/MgO. Spectra are simulated with according to methods described elsewhere.<sup>5</sup>

		Forward reaction		Reverse	Reverse reaction	
Entry	Catalyst	А	Ea	А	Ea	comment
		(kPa <sup>-1</sup> s <sup>-1</sup> )	(kJ mol⁻¹)	(S <sup>-1</sup> )	(kJ mol⁻¹)	
1	Ru/Y <sub>2</sub> O <sub>3</sub>	410	97.6 ± 10	1.5·10 <sup>10</sup>	151.4	This work
2	Ru/CeO <sub>2</sub>	263	69 ± 12	1.5·10 <sup>10</sup>	160.2	This work
3	Ru/MgO	112	152.9 ± 18	1.5·10 <sup>10</sup>	165.3	This work
4	Ru/MgO	56	60.9	1.5·10 <sup>10</sup>	158	Previous work <sup>6</sup>
5	Cs-Ru/MgO	56	33	2.0·10 <sup>10</sup>	137	Previous work <sup>6</sup>
6	Ru/C12A7:e <sup>-</sup>	n.a.	n.a.	n.a.	64	Previous work <sup>13</sup>
7	Ru/C12A7:O <sup>2-</sup>	n.a.	104	n.a.	133	Previous work <sup>17</sup>

**Table S4.** Kinetic results from temperature programmed adsorption (TPA) and temperature programmed desorption (TPD) results.

Entry	Catalyst	ΔH	ΔS	$\Delta G^0$	comment
		(kJ mol⁻¹)	(J K <sup>-1</sup> mol <sup>-1</sup> )	(kJ mol⁻¹)	
1	Ru/Y <sub>2</sub> O <sub>3</sub>	-82.8	-148.5	-39.0	This work
2	Ru/CeO <sub>2</sub>	-62.7	-144.8	-19.5	This work
3	Ru/MgO	-12.3	-161.3	36	This work
4	Ru/MgO⁵	-97.4	-161	-49.4	Previous work <sup>6</sup>
5	Ru/C12A7:O <sup>2-</sup>	-29	n.a.	n.a.	Previous work <sup>17</sup>

**Table S5.** Thermodynamic parameters found for N<sub>2</sub> adsorption according to data represented in **Table S4**.

## 5. Rate controlling typical for the Sabatier optimum

In general, the mechanistic transformation of N<sub>2</sub> to NH<sub>3</sub> can be divided into two steps. The first step consists of the dissociative adsorption of N<sub>2</sub>, whilst the second step is the formation of NH<sub>3</sub><sup>\*</sup> (via step wise protonation) and the consecutive desorption of NH<sub>3</sub>.<sup>18, 19</sup> As the activation barrier for both steps can be related to the binding strength of N\* (atomic nitrogen bound to the catalysts surface), it can be deduced that a low binding strength of N\* (high catalyst support descriptor (CSD) values) results in a low coverage of N<sup>\*</sup>, thus limiting the rate of transformation to the dissociative adsorption of  $N_{2.9}$ , <sup>19-22</sup> In this scenario, increasing the partial pressure of H<sub>2</sub> leads to an increased coverage with H\*, removing available sites for N\* thus reducing the rate of transformation. Consequently, an order  $\leq 0$ can be expected for  $H_2$ .<sup>7</sup> On the other extreme, N\* displays a high binding strength (low CSD values), thus a high coverage of N\* is to be expected and thus the rate of transformation is limited to the consumption of N\* (the step wise protonation of N\* to  $NH_3^*$  and release of  $NH_3^*$ . Here an order  $\ge 0$  for H<sub>2</sub> is to be expected as the coverage of H\* is increased thus facilitating the protonation of N\*.<sup>7, 18, 19</sup> Near or at the Sabatier optimum a clear determination of the rate determined step (RDS) is not possible but should rather be investigated by the degree of rate control.<sup>18, 19, 23-26</sup> Whilst with catalysts far from the Sabatier optimum the RDS can usually be subscribed to a single step (the degree rate control is  $X_{DRC} \approx 1$  for one step), near or at the Sabatier optimum the rate of transformation is defined by two or more steps and the degree of rate control is not near unity for either of the limiting steps.<sup>18,</sup> <sup>24-26</sup> Furthermore, the degree of rate control is dependent on the applied reaction conditions, such as a pressure and temperature etc.<sup>19, 23, 26</sup> Applied to the ammonia synthesis, this translates to a relatively low concentration (high compared to catalysts with weak binding strengths of N\*) at low partial pressures of N<sub>2</sub> and high partial pressure of H<sub>2</sub>.<sup>7</sup> Here the overall transformation is limited by the dissociative adsorption of N<sub>2</sub> and the order of H<sub>2</sub> is  $\leq 0$  but when the partial pressure of H<sub>2</sub> is decreased, the coverage of N\* increases and the stepwise protonation N\* becomes rate controlling, thus resulting in a rate order  $\geq 0$  for H<sub>2</sub>.<sup>7, 9, 18, 24, 26</sup>

Both the study of the apparent activation Energy  $(E_{app})$  in dependence of the CSD developed in this work and the study of the partial pressure onto the overall rate of transformation suggest that our descriptor can be used analogously to the binding strength of N\* used in earlier studies.<sup>7, 9, 19-22</sup> For

instance,  $E_{app}$  of 76 kJ mol<sup>-1</sup> and the fluctuation in the degree in rate control observed for  $Ru@Y_2O_3$ , suggest that  $Ru@Y_2O_3$  possess electronic properties close to those expected for a catalyst near to the Sabatier optimum.<sup>7, 18, 24, 26, 27</sup> Finally, increasing the CSD values lead to a linearly increased of  $E_{app}$  values and the dissociative  $N_2$  adsorption becomes rate controlling (as indicated by the effect of partial pressure of  $H_2$  onto the rate) with a similar behaviour to be expected for lowering the binding strength of N<sup>\*</sup>.<sup>7</sup>

## 6. Estimation of Surace sites in Ru nanoclusters

All calculations assume spheres for the here investigated Ru nanoclucsters.

The volume of a Ru nanocluster is given by

$$V = \frac{\pi d^3}{6}$$

Where d is the diameter of a given nanocluster. The volume of the sub-surface layer of a nanocluster can be calculated accordingly as:

$$V = \frac{\pi (d - 2d_{Ru})^3}{6}$$

Where  $d_{Ru}$  is the atomic diameter of a Ru atom. The density of Ru is given by 12.364 g cm<sup>-3</sup>. Therefore, there are 73.67 atoms nm<sup>-3</sup>. Consequently, the number of atoms in a whole nanocluster and the subsurface can be calculated. With both values the surface Ru atoms can be calculated according to:

$$Ru_{surf} = Ru_{NP} - Ru_{sub}$$

Where  $Ru_{surf}$  are the Ru atoms on the NP surface;  $Ru_{Np}$  are the Ru atoms in the whole nanocluster and  $Ru_{sub}$  are the Ru atoms sub surface. To validate our findings using the diameter of the Ru NP we conducted CO pulse sorption experiments with Ru/CeO<sub>2</sub> and Ru/MgO. Both validation experiments confirm the dispersion found via the nanocluster diameter. The table below summarises all the results.

For a hemisphere, both the total volume and the volume of the subsurface are halved. Note the difference between assuming a sphere and a hemisphere: assuming a sphere does not significantly change the dispersion levels.

Entry	Catalyst	Ru NP diameter (nm)	Dispersion by diameter (sphere)	Dispersion by diameter (hemisphere)	Dispersion by CO pulse sorption
1	Ru/MgO	2.2	0.57	0.59	0.61
2	$Ru/CeO_2$	2.3	0.55	0.55	0.56
3	$Ru/Y_2O_3$	2.3	0.55	0.55	-
4	$Ru/La_2O_3$	3.4	0.40	0.40	-
5	$Ru/Sc_2O_3$	1.8	0.65	0.65	-

Table S6. Dispersion of the Ru nanocluster on the here investigated catalytic materials.

## 7. Pre-exponential factors and other effects affecting the overall rate

Entry	Catalyst	In(A)
1	Ru/Y <sub>2</sub> O <sub>3</sub>	11.5
2	Ru/La <sub>2</sub> O <sub>3</sub>	13.7
3	Ru/CeO <sub>2</sub>	16.4
4	Ru/Sc <sub>2</sub> O <sub>3</sub>	16.1
5	Ru/MgO	26.1

**Table S7.** Pre-exponential factors found for the catalysts.

It is worth pointing out that the concentration of surface sites within the samples varies, which manifests itself in a differing pre-exponential factor. Furthermore, the pre-exponential factor depends on the concentration of catalytic intermediates on the Ru surface, which also varies. These two factors explain the difference in pre-exponential, as found in Table S7.



8. Comparison of Ru nanoclusters before and after the reaction

**Figure S18.** Comparison of Ru nanoclusters deposited onto (a) MgO, (b)  $Sc_2O_3$  (c)  $Y_2O_3$ , (d)  $La_2O_3$  and (e)  $CeO_2$  before and after ammonia synthesis at 400°C and 20 bar for 58h. No significant changes in the Ru particle size are observed.

## 8. References

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