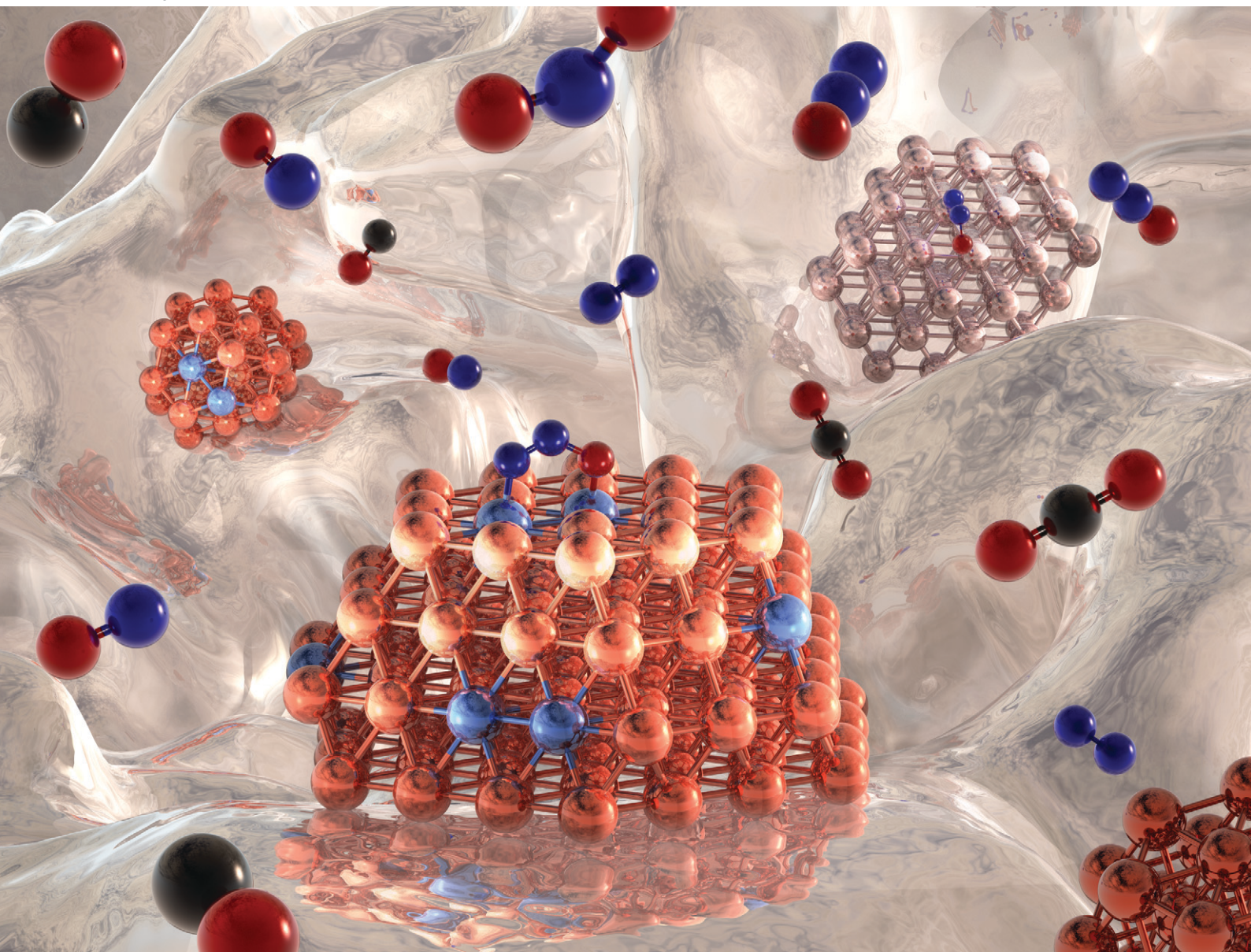


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## PAPER

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# The catalytic decomposition of nitrous oxide and the NO + CO reaction over Ni/Cu dilute and single atom alloy surfaces: first-principles microkinetic modelling†

Konstantinos G. Papanikolaou  and Michail Stamatakis \*

The development of platinum group metal-free (PGM-free) catalysts, which can efficiently reduce pollution-causing emissions, is an important task for overcoming major environmental challenges. In particular, nitrogen oxides (NO<sub>x</sub>) are major contributors to air pollution, being one of the culprits for smog and ozone depletion. In this work, we employ density functional theory (DFT) and microkinetic modelling to investigate the decomposition of N<sub>2</sub>O and the NO + CO reaction over two PGM-free Ni/Cu dilute alloys. On the first surface, Ni atoms are isolated on the host Cu(111), thereby forming a single atom alloy surface (*i.e.* Ni/Cu(111) SAA), while on the second, the same atoms are organised as Ni–Ni dimers (*i.e.* Ni<sub>2</sub>Cu(111)). The same reactions are also simulated on pure Cu(111) (*i.e.* the host surface), and on Rh(111), which is used for benchmarking as Rh is a well-established PGM in emissions control catalysis. Our results suggest that the addition of trace amounts of Ni on Cu(111) may bring about significant improvement to the catalytic performance with regard to the catalytic decomposition of N<sub>2</sub>O. Additionally, we determine that Ni<sub>2</sub>Cu(111) shows equivalent, or under some circumstances even better, performance as compared to Rh(111) for the NO + CO reaction. This work contributes to the long-standing efforts toward the design of efficient PGM-free catalytic materials for the reduction of noxious gases.

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## 1. Introduction

The catalytic reduction of nitric oxide (NO) and the decomposition of nitrous oxide (N<sub>2</sub>O) are reactions of central significance for the prevention and mitigation of critical environmental problems. The emissions of these molecules are, to a large extent, associated with automobiles,<sup>1</sup> which are equipped with the so-called three way catalyst (TWC). TWCs are composed of a complex mixture of oxides (*e.g.* γ-Al<sub>2</sub>O<sub>3</sub>, BaO), whereon noble metals Rh, Pt and Pd are deposited and “undertake” the task of converting noxious gases (*e.g.* CO, NO, N<sub>2</sub>O, C<sub>x</sub>H<sub>y</sub>) into environmentally acceptable products (*i.e.* N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>).

The catalytic reduction of NO by CO is a crucial reaction for controlling automobile emissions, and Rh is regarded as the most promising platinum group metal (PGM) to this end.<sup>1</sup> By and large, this is because Rh can activate the N–O bond at relatively low temperatures<sup>2–4</sup> (the cleavage of this

bond is in many cases the rate determining step of the NO + CO reaction<sup>5,6</sup>), and also because of its high resistance to common poisons (*e.g.* sulphur).<sup>7</sup> As a result, the mechanism and kinetics of the NO + CO reaction over Rh catalysts have been the subject of extensive research for several experimental,<sup>8–14</sup> and theoretical studies.<sup>15–19</sup>

Although Rh exhibits the best performance among other PGMs toward the reduction of NO, its high cost and limited resources are major shortcomings.<sup>1</sup> Unsurprisingly, these downsides have turned the attention of the catalysis community into the search of TWCs that are either PGM-free<sup>20–29</sup> or utilise minimal amounts of PGMs.<sup>30–33</sup> For example, Asakura *et al.* showed that a NiCu/Al<sub>2</sub>O<sub>3</sub> alloy catalyst exhibits distinct catalytic behaviour compared to its Cu/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> monometallic counterparts.<sup>21</sup> The three materials were subject to alternating lean–rich cycles similar to those a TWC may experience during operation. The performance of the Ni-based catalyst deteriorated considerably within the first lean–rich cycle; the Cu-based catalyst was found to be susceptible to oxidation, thereby losing its activity within short time under lean conditions. By contrast, the NiCu/Al<sub>2</sub>O<sub>3</sub> catalyst retained very high N<sub>2</sub> productivity for large time intervals even under lean conditions, and could rapidly self-regenerate (*i.e.* transition

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from an oxide state to the corresponding metallic state) in the beginning of each rich period. The authors ascribed the self-regenerative property of NiCu/Al<sub>2</sub>O<sub>3</sub> to the coexistence of Ni and Cu oxide species that remained in close contact at the end of lean periods.<sup>21</sup> Tanaka and co-workers reported that the same bimetallic alloy supported on a Mg–Al mixed oxide serves as an efficient catalyst for hydrocarbon oxidation (*i.e.* another important reaction that happens over TWCs), under both reducing and oxidative atmospheres.<sup>20</sup> Xing *et al.* synthesised a highly dilute PdCu/Al<sub>2</sub>O<sub>3</sub> catalyst, whereby Pd atoms were atomically dispersed on the Cu host.<sup>33</sup> This catalyst not only showed excellent stability during the NO + CO reaction, but also was able to convert fully NO to N<sub>2</sub> at relatively low temperatures (473 K).

In our recent theoretical work, we screened a number of dilute alloys for their performance on catalysing important “elementary” steps for the NO + CO reaction (*e.g.* direct NO dissociation, N<sub>2</sub> association and CO oxidation).<sup>4</sup> According to our results, a Ni<sub>2</sub>Cu alloy, where Ni atoms are organised as Ni–Ni dimers over the Cu host surface, is promising in activating the N–O bond and is capable of performing facile N<sub>2</sub> association.<sup>4</sup> In particular, Ni<sub>2</sub>Cu exhibited the best performance among the investigated bimetallic surfaces, and similar, or in many cases even better, performance than the PGMs in TWCs (*i.e.* Rh, Pd and Pt). Finally, we argued that this alloy might, in practice, exhibit bifunctional behaviour,<sup>34</sup> where Ni sites cleave N–O bonds, while Cu sites serve as the loci for the oxidation of CO.<sup>35</sup>

In this paper, we employ density functional theory (DFT) and investigate in detail two very relevant reactions to the NO + CO chemistry over Ni/Cu(111) single atom and Ni<sub>2</sub>Cu(111) dilute alloy surfaces; these are the formation and decomposition of N<sub>2</sub>O\*, in particular, NO\* + N\* ↔ N<sub>2</sub>O\* and N<sub>2</sub>O\* ↔ N<sub>2</sub>\* + O\*, respectively, where \* denotes an adsorbed species. Besides their relevance to the catalytic reduction of NO by CO (N<sub>2</sub>O is an exhaust gas and an adduct of catalytic surface chemistry),<sup>36</sup> these reactions are also of general interest.<sup>37</sup> This is because N<sub>2</sub>O is a potent greenhouse gas and an undesired by-product of large-scale processes like the production of adipic and nitric acid.<sup>38</sup> The same reactions are studied over Rh(111), which is used for benchmarking, and also over Cu(111), which is the corresponding host metal surface. We identify different pathways for the activation of N<sub>2</sub>O\* over all surfaces, and we demonstrate that the selectivity of this reaction can be tuned based on the size of the Ni cluster. Importantly, our calculations imply that the presence of small amounts of Ni on Cu(111) strengthens the binding of N<sub>2</sub>O\* to the surface, thereby preventing its desorption and promoting its dissociation. Finally, using the obtained DFT energetics we parameterise a microkinetic model for the NO + CO reaction over the four (111) surfaces. Our theoretical studies aim at providing a first assessment for the performance of the Ni/Cu dilute alloys toward the aforementioned reaction. These simulations reveal that the performance of Ni<sub>2</sub>Cu(111) is certainly superior compared to that of Cu(111) and closely comparable to that of Rh(111). On

this basis, the present study highlights the potential of well-engineered Ni<sub>2</sub>Cu alloys, which are composed of inexpensive and abundant metals, for emissions control technologies.

## 2. Methods

### Density functional theory

Periodic DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) version 5.4.1.<sup>39,40</sup> Exchange and correlation effects were treated with the optB86b-vdW functional,<sup>41,42</sup> which captures van der Waals (vdW) interactions.<sup>43,44</sup> The latter are important to our work and recent studies have shown that the inclusion of dispersion forces in DFT calculations may increase the binding strength of loosely bound adsorbates of the NO + CO reaction (*i.e.* N<sub>2</sub>O\*, CO<sub>2</sub>\*) by as much as 0.7 eV.<sup>16</sup> A kinetic energy cut-off of 400 eV was used for the plane wave basis set that was adopted to describe the wave functions of valence electrons. The interactions between core and valence electrons were modelled by the projector augmented wave (PAW) method.<sup>45</sup> The electronic wave function was converged to 10<sup>−7</sup> eV, and the structures were relaxed until the forces on each atom were less than 0.01 eV Å<sup>−1</sup>. The optB86b-vdW-computed lattice constants are 3.608 Å and 3.829 Å for Cu and Rh, respectively; these values agree well with the corresponding experimental values (3.596 Å and 3.793 Å for Cu and Rh, respectively).<sup>46</sup> The metal surfaces were modelled by a 3 × 3 cell with 5 layers, of which the two bottom ones were fixed at the corresponding lattice constant, thereby simulating the bulk of the material, while the three top layers and any adsorbate atoms were relaxed during geometry optimisation. The Brillouin zone was sampled using a 9 × 9 × 1 Monkhorst–Pack *k*-point mesh.<sup>47</sup> The adsorption energy of N<sub>2</sub>O was computed based on the following equation:

$$E_{\text{ads}}(\text{N}_2\text{O}) = E_{\text{tot}}^{\text{N}_2\text{O}+\text{Slab}} - E_{\text{tot}}^{\text{Slab}} - E_{\text{tot}}^{\text{N}_2\text{O}(\text{g})}, \quad (1)$$

where  $E_{\text{tot}}^{\text{N}_2\text{O}+\text{Slab}}$ ,  $E_{\text{tot}}^{\text{Slab}}$  and  $E_{\text{tot}}^{\text{N}_2\text{O}(\text{g})}$  are the total DFT energies for a slab with an N<sub>2</sub>O\* thereon, a clean slab, and an N<sub>2</sub>O molecule in the gas phase, respectively (the pertinent results are reported in Table 1). The reported transition states were first approached using the dimer method,<sup>48</sup> fully converged with Newton's method, and verified by vibrational analyses, making sure that all the reported transition states had only one imaginary vibrational frequency. The reported activation barriers were computed as  $E_a = E_{\text{TS}} - E_{\text{IS}}$ , where  $E_{\text{TS}}$  and  $E_{\text{IS}}$  are the DFT energies of the transition and initial states, respectively. Vibrational frequencies were computed within the harmonic approximation where the energy of the system is expressed as a Taylor expansion that includes up to second order terms, and the second derivative was estimated within the finite-difference approximation with a displacement of 0.02 Å.

### Microkinetic modelling

The microkinetic model for the NO + CO reaction included 16 reaction steps for Cu(111), Ni/Cu(111) single atom alloy (SAA),



**Table 1** Adsorption energies (in eV) and bond distances (in Å) for the N<sub>2</sub>O\* adsorption geometries over the investigated surfaces. The adsorption energies and bond distances that correspond to the most stable adsorption structure(s) for each surface are shown in bold. A dash indicates either that the adsorption structure is not stable on the specific surface or that it is not a minimum on the potential energy surface (i.e. there was an imaginary frequency in the vibrational analysis). For comparison:  $d_{\text{N-N}} = 1.14$  Å and  $d_{\text{N-O}} = 1.20$  Å for gas N<sub>2</sub>O (ref. 63)

Adsorption structure	Property	Rh(111)	Cu(111)	Ni/Cu(111) SAA	Ni <sub>2</sub> Cu(111)
η1-(N <sub>f</sub> {top}) (denoted as η1)	$E_{\text{ads}}(\text{N}_2\text{O})$	-0.71	-0.21	<b>-0.70</b>	-0.68
	$d_{\text{N-O}}$	1.20	1.20	<b>1.20</b>	1.21
	$d_{\text{N-N}}$	1.15	1.15	<b>1.15</b>	1.15
η2-f(N <sub>f</sub> {bridge}, N <sub>c</sub> {top}) (denoted as η2NbNt)	$E_{\text{ads}}(\text{N}_2\text{O})$	<b>-0.83</b>	+0.15	-0.43	<b>-0.74</b>
	$d_{\text{N-O}}$	<b>1.22</b>	1.23	1.23	<b>1.23</b>
	$d_{\text{N-N}}$	<b>1.35</b>	1.29	1.29	<b>1.31</b>
η2-(N <sub>f</sub> {top}, O{top}) (denoted as η2NtOt)	$E_{\text{ads}}(\text{N}_2\text{O})$	-0.72	-0.20	-0.53	-0.68
	$d_{\text{N-O}}$	1.33	1.28	1.30	1.32
	$d_{\text{N-N}}$	1.20	1.19	1.20	1.20
η2-(N <sub>f</sub> {hcp}, O{top})	$E_{\text{ads}}(\text{N}_2\text{O})$	—	<b>-0.25</b>	-0.44	<b>-0.73</b>
	$d_{\text{N-O}}$	—	<b>1.30</b>	1.31	<b>1.32</b>
	$d_{\text{N-N}}$	—	<b>1.27</b>	1.25	<b>1.27</b>

and Ni<sub>2</sub>Cu(111) surfaces and 14 reaction steps for Rh(111) – (see Table 2). On the monometallic surfaces there was only one site type, while in the bimetallic surfaces there were Cu and Ni sites, denoted as Cu\* and Ni\*, respectively. Therefore, for the latter surfaces, we define the “local” coverages as follows:

$$\theta_i^{(m)} = \frac{N_i^{(m)}}{N_{\text{sites}}^{(m)}}, \quad (2)$$

where  $N_i^{(m)}$  is the number of molecules of adsorbate species  $i$  that are bound to sites of type  $m$  (either Cu\* or Ni\*); and  $N_{\text{sites}}^{(m)}$  is the number of sites of type  $m$ . We further define the *total* coverage of adsorbate  $i$ ,  $\theta_i$ , as:

$$\theta_i = \sum_{m=1}^{N_{\text{st}}} x_m \theta_i^{(m)}, \quad (3)$$

where  $N_{\text{st}}$  is the total number of site types; the summation index  $m$  runs over these site types (for the bimetallic surfaces the two types are: Cu\* and Ni\*; for monometallic surfaces there

is only one site type which can be either Cu\* or Rh\*); and  $x_m$  is the fraction of sites  $m$  on the surface, given as:

$$x_m = \frac{N_{\text{sites}}^{(m)}}{\sum_{\ell=1}^{N_{\text{st}}} N_{\text{sites}}^{(\ell)}}. \quad (4)$$

All reactions were considered reversible, and the forward/reverse rates were given by the typical mass-action law expressions used in microkinetic models, which contain the partial pressures of gas-phase species (considered as constants) and the surface coverages. The gas-phase species taken into account were NO, CO, N<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, while the surface species were O\*, CO\*, N\*, NO\*, CO\*, N\* and N<sub>2</sub>O\*, as well as the vacant site pseudo-species denoted as \*. Regarding the N<sub>2</sub>O\* species, three different adsorption geometries were taken into account (see the next section). The transitions from one adsorption geometry to another could happen through *transformation reactions* that were included in the reaction

**Table 2** Reaction mechanism for the NO + CO reaction, and the corresponding forward ( $E_{\text{fwd}}$ ) and reverse ( $E_{\text{rev}}$ ) barriers (in eV). All reactions are treated as reversible, and dashes mean that the corresponding reaction does not take place on the catalyst surfaces. R1–R7 correspond to molecular adsorptions/desorptions; R8–R16 are surface reactions from which R10 and R11 are N<sub>2</sub>O\* transformation reactions

Reaction & reaction number		Rh(111)		Cu(111)		Ni/Cu(111) SAA		Ni <sub>2</sub> Cu(111)	
		$E_{\text{fwd}}$	$E_{\text{rev}}$	$E_{\text{fwd}}$	$E_{\text{rev}}$	$E_{\text{fwd}}$	$E_{\text{rev}}$	$E_{\text{fwd}}$	$E_{\text{fwd}}$
NO <sub>(g)</sub> + * ↔ NO*	(R1)	0.00	2.87	0.00	1.55	0.00	2.10	0.00	2.65
CO <sub>(g)</sub> + * ↔ CO*	(R2)	0.00	2.20	0.00	0.78	0.00	1.51	0.00	1.71
N <sub>2(g)</sub> + * ↔ N <sub>2</sub> *	(R3)	0.00	0.79	0.00	0.15	0.00	0.79	0.00	0.77
CO <sub>2(g)</sub> + * ↔ CO <sub>2</sub> *	(R4)	0.00	0.27	0.00	0.30	0.00	0.28	0.00	0.37
N <sub>2</sub> O <sub>(g)</sub> + * ↔ N <sub>2</sub> O* η2NbNt	(R5)	0.00	0.83	0.00	0.00	0.00	0.43	0.00	0.74
N <sub>2</sub> O <sub>(g)</sub> + * ↔ N <sub>2</sub> O* η2NtOt	(R6)	0.00	0.72	0.00	0.20	0.00	0.53	0.00	0.68
N <sub>2</sub> O <sub>(g)</sub> + * ↔ N <sub>2</sub> O* η1	(R7)	0.00	0.71	0.00	0.21	0.00	0.70	0.00	0.68
NO* + * ↔ N* + O*	(R8)	1.42	2.03	1.57	1.43	1.47	1.43	1.30	1.24
NO* + N* ↔ N <sub>2</sub> O* η2NbNt + *	(R9)	1.50	0.40	0.44	0.94	0.51	0.45	0.60	0.68
N <sub>2</sub> O* η2NbNt ↔ N <sub>2</sub> O* η1	(R10)	0.46	0.30	0.14	0.56	0.24	0.50	0.37	0.31
N <sub>2</sub> O* η1 ↔ N <sub>2</sub> O* η2NtOt	(R11)	0.24	0.40	0.06	0.05	0.29	0.12	0.32	0.32
N <sub>2</sub> O* η2NtOt + * ↔ N <sub>2</sub> * + O*	(R12)	0.07	2.54	0.05	2.12	0.03	2.26	0.09	2.48
N <sub>2</sub> O* η2NbNt + * ↔ N <sub>2</sub> * + O*	(R13)	—	—	0.19	2.20	0.23	2.56	0.23	2.51
CO* + O* ↔ CO <sub>2</sub> * + *	(R14)	1.17	0.41	0.48	1.22	0.71	0.60	0.88	0.48
NO* + NO* ↔ N <sub>2</sub> O* η1 + O*	(R15)	—	—	0.84	1.82	1.27	1.60	1.30	1.69
N* + N* ↔ N <sub>2</sub> *	(R16)	1.85	2.14	0.64	3.6	0.88	3.40	0.62	2.81



mechanism (see R10–R11 in Table 2). The forward rate for reaction  $j$  on site-type  $m$  is formulated as follows:

$$R_{\text{fwd},j}^{(m)} = k_{\text{fwd},j}^{(m)} \prod_{g \in \mathcal{R}_j^{\text{gas}}} (P_g)^{-\nu_{gj}} \prod_{i \in \mathcal{R}_j^{\text{surf}}} \left( \theta_i^{(\mu_{ij})} \right)^{-\nu_{ij}} \quad (5)$$

In the above equation,  $\mathcal{R}_j^{\text{gas}}$  is the set of gas-phase reactant species of reaction  $j$ ;  $P_g$  is the partial pressure of gas species  $g$ ; and  $\nu_{gj}$  is the stoichiometric coefficient of that gas phase species in reaction  $j$ . By convention, stoichiometric coefficients are negative for reactants and positive for products; if a species does not appear in a certain reaction, the corresponding stoichiometric coefficient is zero. Moreover,  $\mathcal{R}_j^{\text{surf}}$  is the set of surface reactant species of reaction  $j$ ;  $\nu_{ij}$  is the stoichiometric coefficient of surface species  $i$  in reaction  $j$ ; and  $\theta_i^{(\mu_{ij})}$  is the local coverage of surface species  $i$  on sites of type  $\mu_{ij}$ . The latter term may or may not be equal to  $m$ , since, a reaction that is said to happen on site  $m$  (e.g. Ni\*), may well involve another species adsorbed on a neighbouring site type (e.g. Cu\*). For instance, when reaction R9 of Table 2 ( $\text{NO}^* + \text{N}^* \leftrightarrow \text{N}_2\text{O}^* + *$ ) happens on a Ni site,  $\text{NO}^*$  is found on the Ni site, while  $\text{N}^*$  is on Cu; therefore, the rate would be:

$$R_{\text{fwd},9}^{(\text{Ni}^*)} = k_{\text{fwd},9}^{(\text{Ni}^*)} \theta_{\text{NO}^*}^{(\text{Ni}^*)} \theta_{\text{N}^*}^{(\text{Cu}^*)}.$$

For further information on the considered reactant configurations for events that involve two sites see Table S3 in the ESI.† Similarly, the reverse rate for reaction  $j$  on site-type  $m$  is formulated as follows:

$$R_{\text{rev},j}^{(m)} = k_{\text{rev},j}^{(m)} \prod_{g \in \mathcal{P}_j^{\text{gas}}} (P_g)^{\nu_{gj}} \prod_{i \in \mathcal{P}_j^{\text{surf}}} \left( \theta_i^{(\mu_{ij})} \right)^{\nu_{ij}} \quad (6)$$

Note that  $\mathcal{P}_j^{\text{gas}}$  and  $\mathcal{P}_j^{\text{surf}}$  denote sets of products of reaction  $j$ , and the stoichiometric coefficients appear with their “original” positive signs, because of the convention mentioned earlier.

The rate constant calculations for the surface reactions ( $k_{\text{fwd},j}^{(m)}$  and  $k_{\text{rev},j}^{(m)}$ ) are calculated after invoking widely used transition state theory approximations. If a reaction cannot happen on a certain site, then  $k_{\text{fwd},j}^{(m)} = k_{\text{rev},j}^{(m)} = 0$ . We further define the net rate of reaction  $j$  on site  $m$  as:

$$R_j^{(m)} = R_{\text{fwd},j}^{(m)} - R_{\text{rev},j}^{(m)} \quad (7)$$

The coverage profiles over the investigated surfaces can now be obtained by solving a system of ordinary differential equations (ODEs) written as

$$\frac{d\theta_i^{(m)}}{dt} = \sum_{j=1}^{N_R} \nu_{ij} R_j^{(m)}, \quad (8)$$

where  $N_R$  is the total number of (reversible) reactions. The ODEs were solved in Matlab R2017a, using the ode23s solver, which is capable of dealing with stiff equations. An

important constraint that had to be satisfied is the *site conservation law*

$$\sum_{i=1}^{N_s} \sum_{m=1}^{N_{\text{st}}} x_m \theta_i^{(m)} = 1. \quad (9)$$

To calculate the rate constants of the reactions the following assumptions and approximations were adopted. Molecular adsorptions were assumed as non-activated events with a 2D gas as a transition state, where molecules retain translational and rotational degrees of freedom. Accordingly, the rate constants for molecular adsorptions were calculated using the Hertz–Knudsen equation assuming a sticking coefficient equal to unity (eqn (10)):<sup>49</sup>

$$k_{\text{ads}} = \frac{A_{\text{st}}}{\sqrt{2 \cdot \pi \cdot m_i \cdot k_B \cdot T}}, \quad (10)$$

where  $m_i$  is the mass of molecule  $i$ ;  $k_B$  is the Boltzmann constant;  $T$  is the temperature; and  $A_{\text{st}}$  is the effective area of the adsorption site. The pressure of gas phase-species is omitted in eqn (10) because it is explicitly taken into account in eqn (5) and (6). The rate constants for surface reactions and desorption events were calculated using the Eyring equation:<sup>50</sup>

$$k_{\text{fwd/rev},j}^{(m)} = \frac{k_B T}{h} \frac{Q^{\text{TS}}}{Q^{\text{IS}}} \exp \left( -\frac{E_{\text{a,fwd/rev},j}^{(m)}}{k_B T} \right), \quad (11)$$

where  $h$  is the Planck's constant;  $Q^{\text{TS}}$  and  $Q^{\text{IS}}$  are the partition functions of the transition and initial states, respectively. The rate constants of surface reactions were calculated using the harmonic approximation, and therefore frustrated translations and rotations of surface species were treated as vibrations; under these circumstances, the partition function of an adsorbed state (either initial or transition state) is equal to the vibrational partition function ( $q_{\text{vib}}$ ):

$$Q \approx q_{\text{vib}} = \prod_{k=1}^S \frac{e^{-\hbar \omega_k / (2k_B T)}}{1 - e^{-\hbar \omega_k / (k_B T)}}, \quad (12)$$

where  $S$  is the number of vibrational modes;  $\omega_k$  is the angular frequency of the  $k$ th normal mode of vibration; and  $\hbar$  is the reduced Planck's constant.

The net rates for  $\text{N}_2$  and  $\text{N}_2\text{O}$  are calculated as follows:

$$R_{\text{N}_2,\text{net}} = \sum_{m=1}^{N_{\text{st}}} R_{\text{R}_3,\text{net}}^{(m)}, \quad (13)$$

$$R_{\text{N}_2\text{O},\text{net}} = \sum_{j=\text{R5}}^{\text{R7}} \sum_{m=1}^{N_{\text{st}}} R_{j,\text{net}}^{(m)}, \quad (14)$$

where  $R_{j,\text{net}}^{(m)}$  is the net reaction rate of  $j$  on site  $m$ . Finally, the contribution of each elementary step to the total reaction rate was quantified using Campbell's degree of rate control (DRC) – (see eqn (15)):<sup>51,52</sup>



$$X_{RC,j}^{(m)} = \frac{k_j^{(m)}}{R_{N_{2,net}}} \left( \frac{\partial R_{N_{2,net}}}{\partial k_j^{(m)}} \right)_{K_\ell^{(n)}, k_{\ell \neq j}^{(n+m)}} = \left( \frac{\partial \ln R_{N_{2,net}}}{\partial \ln k_j^{(m)}} \right)_{K_\ell^{(n)}, k_{\ell \neq j}^{(n+m)}}, \quad (15)$$

where  $X_{RC,j}^{(m)}$  is the DRC coefficient for reaction  $j$  on site  $m$ ;  $R_{N_{2,net}}$  is the net reaction rate for the production of  $N_2$  (eqn (13)) on site  $m$  (eqn (7));  $K_\ell^{(n)}$  is the equilibrium constant of reaction  $\ell = 1, \dots, N_R$  on site  $m = 1, \dots, N_{st}$ ;  $k_{\ell \neq j}^{(n+m)}$  are the rate constants for all other steps than  $j$  that take place on either  $Cu^*$  or  $Ni^*$  (the site other than  $m$ ). The larger the absolute value of  $X_{RC,j}^{(m)}$  the larger the influence of that reaction step to the overall reaction rate; also when  $X_{RC,j}^{(m)} > 0$ , the reaction is rate-limiting, whereas for  $X_{RC,j}^{(m)} < 0$  the reaction is rate-inhibiting.

### 3. Results and discussion

#### 3.1. Adsorption of $N_2O$ on Ni/Cu dilute alloy surfaces

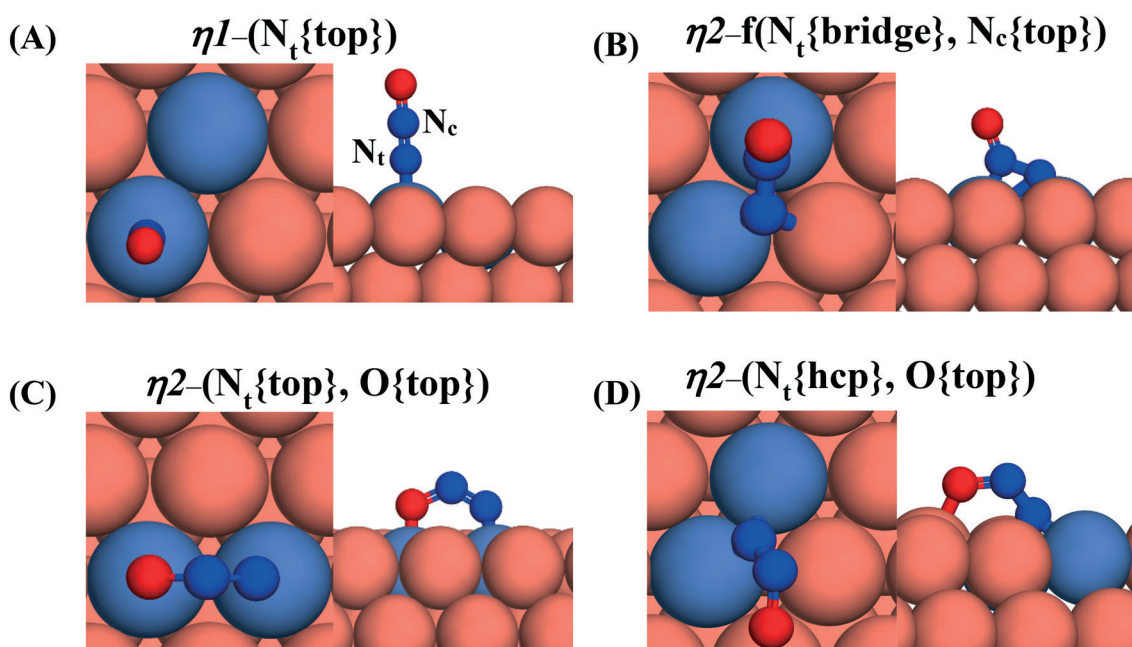
Gas-phase nitrous oxide is a linear molecule ( $C_{\infty V}$  symmetry) and a harmful by-product of industrial processes (e.g. nitric acid production). Its catalytic decomposition has been investigated over many transition metals, including Rh,<sup>53</sup> Cu,<sup>54</sup> Ru,<sup>55</sup> Pd,<sup>56</sup> Fe,<sup>57</sup> Ni,<sup>58</sup> Pt,<sup>59</sup> PdAu,<sup>60</sup> and PdCu.<sup>61</sup> Here, we first examine the adsorption of nitrous oxide on Cu(111), Ni/Cu(111) SAA and  $Ni_2Cu(111)$  surfaces, but also on our “benchmarking surface” Rh(111).

It is known that  $N_2O^*$  may adopt a number of different adsorption geometries upon its interaction with metal surfaces.<sup>56,62</sup> Accordingly, we identify six stable adsorption geometries out of which four are displayed in Fig. 1, while the full list is given in the first section of the ESI† These four adsorption structures are important because they are adopted

by  $N_2O^*$  upon its decomposition to either to  $N_2^* + O^*$  or  $NO^* + N^*$  (see sections 3.2 and 3.3), and are denoted as:  $\eta 1-(N_t\{top\})$ ,  $\eta 2-f(N_t\{bridge\}, N_c\{top\})$ ,  $\eta 2-(N_t\{top\}, O\{top\})$ , and  $\eta 2-(N_t\{hcp\}, O\{top\})$  – (Fig. 1). Since we will be referring often to the first three throughout this paper, we adopt the following abbreviations for them:  $\eta 1$ ,  $\eta 2NbNt$  and  $\eta 2NtOt$ , respectively.

The computed adsorption energies for the four geometries, along with the N–O ( $d_{N-O}$ ) and N–N ( $d_{N-N}$ ) bond distances are summarised in Table 1. We note that the most preferred  $N_2O^*$  adsorption structure on Rh(111) is the  $\eta 2NbNt$  mode ( $E_{ads}(N_2O) = -0.83$  eV) – (Table 1). This type of adsorption can be considered as a weak chemisorption because: (1) the geometry of  $N_2O^*$  deviates noticeably from the gas-phase geometry, which is linear; and (2) because the N–N bond is considerably elongated ( $d_{N-N} = 1.14$  Å and 1.35 Å for gas-phase  $N_2O$  and  $\eta 2NbNt$   $N_2O^*$ , respectively). The following most stable adsorption structures are the  $\eta 1$  and  $\eta 2NtOt$  with  $E_{ads}(N_2O) = -0.71$  eV and  $E_{ads}(N_2O) = -0.72$  eV, respectively. The former structure can be characterised as a strong physisorption owing to the unaffected geometry and bond lengths of  $\eta 1$   $N_2O^*$  as compared to gas-phase  $N_2O$  ( $d_{N-N} = 1.14$  Å and  $d_{N-O} = 1.20$  Å for gas  $N_2O$ ) – (Table 1).

The activation of the N–N bond in the  $\eta 2NbNt$  structure can be elucidated by careful examination of the electronic structure of this geometry (Fig. S2†).<sup>62</sup> Our density of states (DOS) analyses indicate that in  $\eta 2NbNt$  the  $2\pi$  and  $3\pi$  orbitals of  $N_2O^*$  become broader as a result of their interaction with the metal states, whilst the same is not true for the  $\eta 1$  structure where the same orbitals appear rather localised (Fig. S2†). The broadening of the  $3\pi$  orbitals is indicative of electron back-donation, which in turn leads to the activation



**Fig. 1** Top and side views of (A)  $\eta 1-(N_t\{top\})$ ; (B)  $\eta 2-f(N_t\{bridge\}, N_c\{top\})$ ; (C)  $\eta 2-(N_t\{top\}, O\{top\})$  and (D)  $\eta 2-(N_t\{hcp\}, O\{top\})$  adsorption structure. On the side view of (A) we highlight the terminal ( $N_t$ ) and central ( $N_c$ ) nitrogen atoms. Ni, Cu, N and O atoms are shown in purple, orange, blue and red, respectively. The adsorption geometries are shown over  $Ni_2Cu(111)$ , but they are representative for all surfaces.





of the N–N bond. This result is in qualitative agreement with the work of Paul *et al.*<sup>62</sup> where the authors, by means of DFT calculations using the PW91 functional, found that the  $\eta 2\text{NbNt}$  and  $\eta 1$  are *ca.* equally stable on Rh(111) ( $E_{\text{ads}}(\text{N}_2\text{O}) = -0.35$  eV and  $E_{\text{ads}}(\text{N}_2\text{O}) = -0.39$  eV, respectively). Moreover, our calculations suggest that  $\text{N}_2\text{O}^*$  is bound stronger by *ca.* 0.5 eV on Rh(111) compared to the work of Paul *et al.*<sup>62</sup> and this discrepancy may be attributed to the inclusion of nonlocal electron correlation effects in our calculations.<sup>16</sup>

We proceed by investigating the adsorption of  $\text{N}_2\text{O}^*$  over Cu(111) and the Cu-based alloy surfaces where Ni atoms are either distributed as isolated atoms or as Ni–Ni dimers. In general, we find that  $\text{N}_2\text{O}^*$  interacts weakly with Cu(111) (Table 1) and that the most stable adsorption geometries thereon are  $\eta 2\text{-(N}_t\{\text{hcp}\}, \text{O}\{\text{top}\})$  and  $\eta 1$  for which  $E_{\text{ads}}(\text{N}_2\text{O}) = -0.25$  eV and  $-0.21$  eV, respectively. Yet, the presence of a small amount of Ni on the surface layer of Cu(111) brings about drastic changes with regard to the binding strength of  $\text{N}_2\text{O}^*$  (Table 1). Thus, the most stable adsorption geometry on the Ni/Cu(111) SAA surface is  $\eta 1$  ( $E_{\text{ads}}(\text{N}_2\text{O}) = -0.70$  eV), where the  $\text{N}_t$  atom of  $\text{N}_2\text{O}^*$  interacts closely with the isolated Ni atom. By contrast, the  $\eta 2\text{NbNt}$  and  $\eta 2\text{-(N}_t\{\text{hcp}\}, \text{O}\{\text{top}\})$  are the most favourable adsorption modes for  $\text{Ni}_2\text{Cu(111)}$ , with  $E_{\text{ads}}(\text{N}_2\text{O}) = -0.74$  eV and  $E_{\text{ads}}(\text{N}_2\text{O}) = -0.73$  eV, respectively. Crucially, the corresponding adsorption processes are about 0.5 eV more exothermic than the  $\eta 1$  and  $\eta 2\text{-(N}_t\{\text{hcp}\}, \text{O}\{\text{top}\})$  modes on Cu(111), thereby highlighting the potential of the Ni/Cu dilute alloys for the decomposition of  $\text{N}_2\text{O}^*$ . With this in mind, we examine the latter reaction over Cu(111) and the Cu-based surfaces.

### 3.2. $\text{N}_2\text{O}^*$ formation and activation on Cu-based surfaces – the “conventional” reaction path

In order to verify the reliability of our data, we first perform calculations in relation to the activation of  $\text{N}_2\text{O}^*$  on the

Rh(111) surface, and compare our results to those reported in previous theoretical works. The computed reaction pathway for the decomposition of  $\text{N}_2\text{O}^*$  to either  $\text{N}_2^* + \text{O}^*$  or  $\text{NO}^* + \text{N}^*$  is displayed in Fig. S3.† In this “conventional” reaction pathway the transformation of  $\text{NO}^* + \text{N}^*$  to  $\text{N}_2^* + \text{O}^*$  proceeds *via* the  $\eta 1$  adsorption structure (Fig. S3.†), and our computed activation barriers are congruent with previously calculated values. For example, Paul *et al.*<sup>62</sup> reported an activation barrier of 0.34 eV for the transformation of the  $\eta 2\text{NbNt}$  structure to the  $\eta 1$  structure; this number is in good agreement with our computed barrier ( $E_a = 0.38$  eV from state (4) to state (3) in Fig. S3.†). Another example is the required barrier for the decomposition of the  $\eta 2\text{NbNt}$  (state (1) in Fig. S3.†) structure to  $\text{NO}^* + \text{N}^*$ . The values for this work and ref. 62 are 0.36 eV and 0.41 eV, respectively. Consequently, we use our computational setup and study the decomposition of  $\text{N}_2\text{O}^*$  on Cu(111), Ni/Cu(111) SAA and  $\text{Ni}_2\text{Cu(111)}$  surfaces.

Fig. 2(A) shows the “conventional” decomposition pathway for Cu(111), where the  $\eta 1$  structure “connects” the  $\text{NO}^* + \text{N}^*$  and  $\text{N}_2^* + \text{O}^*$  states. During the  $\text{NO} + \text{CO}$  reaction, the combination of  $\text{NO}^*$  and  $\text{N}^*$  species may result in the formation of  $\text{N}_2\text{O}^*$ , which ideally should be decomposed to  $\text{N}_2^* + \text{O}^*$ . Once formed,  $\text{N}_2\text{O}^*$  adopts the  $\eta 2\text{NbNt}$  structure, and starting from this geometry on Cu(111) (state (1) in Fig. 2(A)), we realise that the formation of  $\text{N}_2^*$  and  $\text{O}^*$  is thermodynamically and kinetically favoured over the formation of  $\text{NO}^*$  and  $\text{O}^*$ . In particular, the decomposition of  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  to  $\text{NO}^* + \text{O}^*$  requires the traversing of a barrier of 0.94 eV, while the three barriers to be traversed for the formation of  $\text{N}_2^* + \text{O}^*$  are only 0.14 eV, 0.06 eV and 0.06 eV. Yet, we conjecture that Cu(111) will be susceptible to the production of  $\text{N}_2\text{O}$  during the  $\text{NO} + \text{CO}$  reaction. This is because of the following reasons: (1)  $\text{N}_2\text{O}^*$  can be formed from  $\text{NO}^*$  and  $\text{N}^*$  species with a relatively small kinetic barrier of 0.44 eV (Fig. 2(A)); once  $\text{N}_2\text{O}^*$  is formed from  $\text{NO}^*$  and  $\text{N}^*$  in the  $\eta 2\text{NbNt}$  structure (state (1) in Fig. 2(A)), its

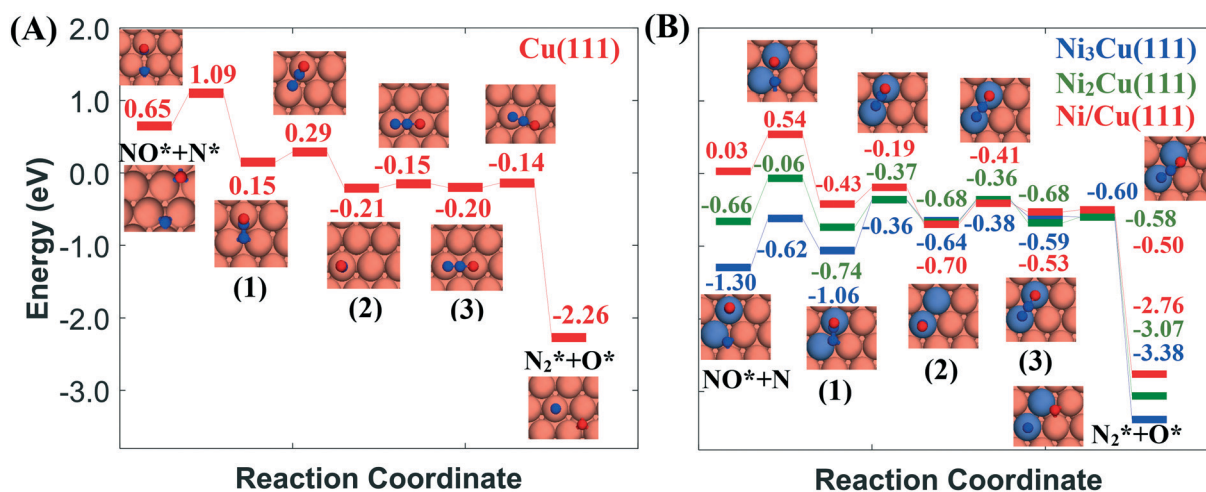


Fig. 2 Reaction path for the decomposition of  $\text{N}_2\text{O}^*$  to  $\text{NO}^* + \text{N}^*$  or  $\text{N}_2^* + \text{O}^*$  over (A) Cu(111) surface; (B) Ni/Cu(111) SAA,  $\text{Ni}_2\text{Cu(111)}$  and  $\text{Ni}_3\text{Cu(111)}$  surfaces. The numbering of the adsorbed configurations of  $\text{N}_2\text{O}$  is as follows: (1)  $\eta 2\text{NbNt}$ , (2)  $\eta 1$  and (3)  $\eta 2\text{NbNt}$ . The zero level corresponds to infinitely separated (and thus non-interacting)  $\text{N}_2\text{O}$  molecule and clean slab. States without any labelling are transition states. Side views of the different states are shown in the ESI.† Ni, Cu, O and N atoms are shown in purple, orange, red and blue, respectively.



desorption is the most probable scenario (Table 1); and (3) even in the  $\eta 1$  and  $\eta 2\text{NbNt}$  geometries,  $\text{N}_2\text{O}^*$  binds weakly on Cu(111) and its desorption will be proceeding at considerable rates even at moderate reaction temperatures.

On the contrary, we find that the decomposition of  $\text{N}_2\text{O}^*$  may be significantly promoted by embedding one or two Ni atoms on Cu(111), thereby forming a single atom alloy or a dilute alloy surface,<sup>64–71</sup> where in the latter case, Ni atoms are organised as dimers or trimers. We note that *ab initio* Monte Carlo simulations predict that small Ni clusters (e.g. Ni–Ni dimers) are abundant in Ni/Cu dilute alloy surfaces under vacuum conditions, while their thermodynamic stability can be further enhanced by exposing the alloy surface to CO at a range of partial pressures that lead to dopant fractional coverages less than 1.<sup>72</sup> The computed desorption energies for  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  (state (1) in Fig. 2(B)) on Ni/Cu(111) SAA and  $\text{Ni}_2\text{Cu}(111)$  are 0.43 eV and 0.74 eV, respectively. By considering this adsorption structure as the starting point, we note that the transformation of  $\text{N}_2\text{O}^*$  to structure  $\eta 1$  (i.e. state (2)) and  $\eta 2\text{NbNt}$  (i.e. state (3)), and the decomposition of the latter to  $\text{N}_2^* + \text{O}^*$  would generally traverse small barriers, which are always less than 0.30 eV and 0.40 eV for Ni/Cu(111) SAA and  $\text{Ni}_2\text{Cu}(111)$ , respectively. Thus,  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  (state (1)) would prefer to decompose to  $\text{N}_2^* + \text{O}^*$ , than desorb to the gas phase (Fig. 2(B)).

The exothermic adsorption of  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  (i.e. the first adopted structure after  $\text{N}_2\text{O}^*$  formation from  $\text{NO}^*$  and  $\text{N}^*$ ) will, to certain extent, prevent the  $\text{N}_2\text{O}^*$  desorption to the gas phase. This will increase the probability of “trapping”  $\text{N}_2\text{O}^*$  to the catalyst surface and therefore the probability for its decomposition. Moreover, even stronger  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  binding should be expected on Ni–Ni dimers and Ni single atoms that are embedded on more open surfaces than the densely packed (111) and on undercoordinated sites that can be found in catalytic nanoparticles.

Another point that merits consideration is that the selectivity toward the decomposition products ( $\text{NO}^* + \text{N}^*$  or  $\text{N}_2^* + \text{O}^*$ ) can be altered by tuning the size of the Ni cluster. To better illustrate this point, we present the corresponding  $\text{N}_2\text{O}^*$  decomposition pathway over a Cu(111) with an embedded Ni trimer ( $\text{Ni}_3\text{-Cu}(111)$  in Fig. 2(B)). Interestingly, the kinetic barrier for the formation of the  $\eta 2\text{NbNt}$  geometry (state (1) in Fig. 2(B)) from  $\text{NO}^*$  and  $\text{N}^*$  increases monotonically at increasing size of the Ni cluster ( $E_a = 0.51$  eV, 0.60 eV and 0.68 eV for Ni/Cu(111) SAA,  $\text{Ni}_2\text{Cu}(111)$  and  $\text{Ni}_3\text{Cu}(111)$ , respectively). The opposite is true for the reverse reaction (i.e.  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  to  $\text{NO}^* + \text{N}^*$ ) for which  $E_a = 0.97$  eV, 0.68 eV and 0.44 eV for Ni/Cu(111) SAA,  $\text{Ni}_2\text{-Cu}(111)$  and  $\text{Ni}_3\text{Cu}(111)$ , respectively. This result underlines the importance of developing ways to control the architecture of dilute alloy surfaces and former studies discuss that this may be achieved under reactive conditions.<sup>72–75</sup>

### 3.3. $\text{N}_2\text{O}$ formation and activation on Cu-based surfaces – an alternative reaction path

Besides the “conventional” route for the decomposition of  $\text{N}_2\text{O}^*$  (Fig. 2), we have identified an alternative reaction

pathway which, to the best of our knowledge, has not been reported before. This path exists only on Cu(111) and on the Ni/Cu dilute alloy surfaces. The decomposition of  $\text{N}_2\text{O}^*$  to  $\text{N}_2^* + \text{O}^*$  happens without transformation to the  $\eta 1$  structure as in the conventional pathway. In contrast, in this pathway the two decomposed states (i.e.  $\text{NO}^* + \text{N}^*$  and  $\text{N}_2^* + \text{O}^*$ ) are “connected” *via* the  $\eta 2\text{-}(\text{N}_{\text{fcc}}, \text{O}_{\text{top}})$  adsorption structure (this is as Fig. 1(D) but over an fcc site; the two adsorption structures exhibit the same binding strength –  $E_{\text{ads}}(\text{N}_2\text{O}) = -0.74$  eV for  $\text{Ni}_2\text{Cu}(111)$ ). After performing a number of test simulations, we could not identify the same path on Rh(111), and this might explain why it was not reported in previous studies.<sup>62</sup>

For all the Cu-based surfaces, Fig. 3 shows that  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  is formed in the same way as in the reaction path of Fig. 2. Then the  $\eta 2\text{NbNt}$   $\text{N}_2\text{O}^*$  rotates around the axis of the N–N bond, thereby bringing the more electronegative O closer to the surface. Interestingly, once O is closer to the Ni/Cu(111) SAA, the N–O bond is immediately cleaved and the kinetic barrier for this process is only 0.23 eV (Fig. 3(B)). The ease by which the N–O is broken over the Ni/Cu SAA surface may be associated with the sharp and narrow distribution of the electron density of the single Ni atom close to the Fermi level,<sup>4,76</sup> and it is expected that back-donation to the  $3\pi$  antibonding orbital of  $\text{N}_2\text{O}^*$  enables the facile activation of the N–O bond.

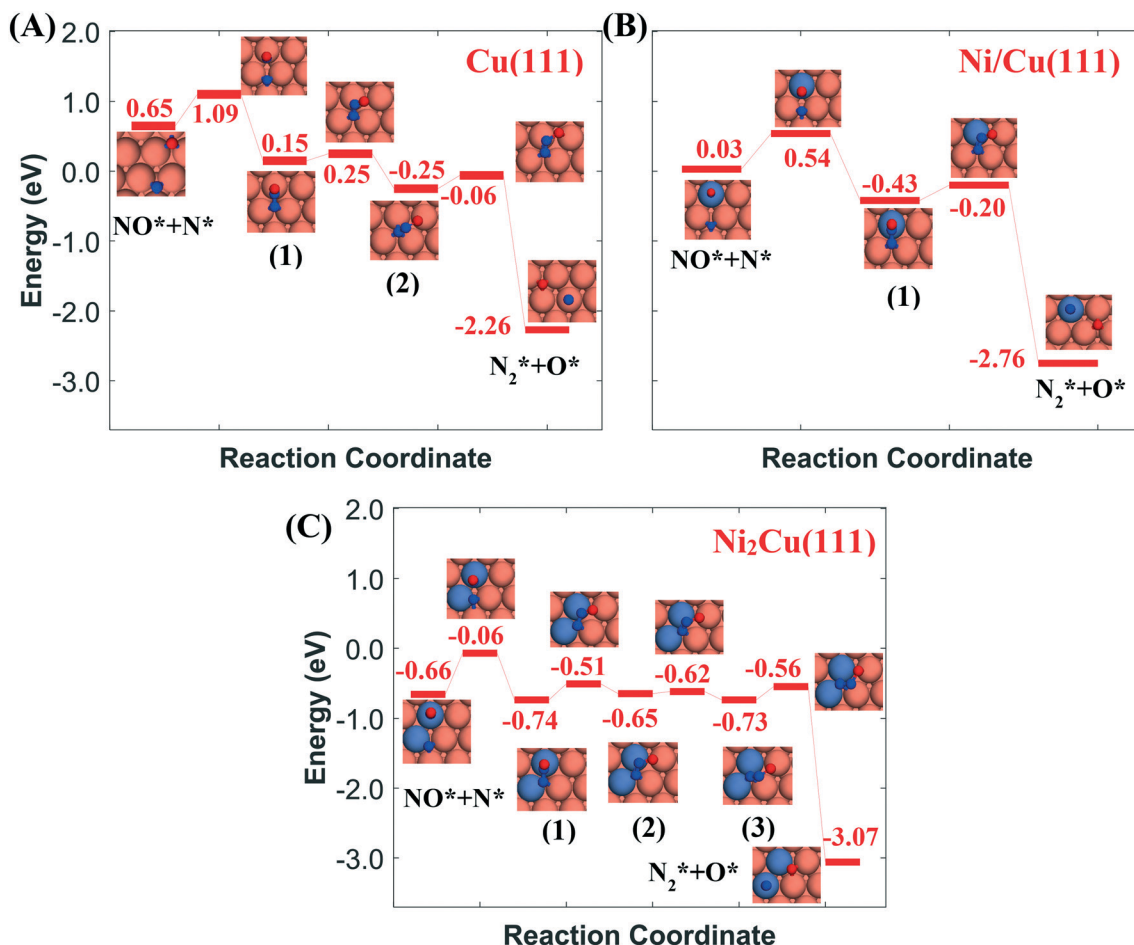
By contrast, the decomposition of  $\text{N}_2\text{O}^*$  to  $\text{N}_2^*$  and  $\text{O}^*$  is taking place through the  $\eta 2\text{-}(\text{N}_{\text{fcc}}, \text{O}_{\text{top}})$  geometry (state (2) and (3) in Fig. 3(A) and (C), respectively) over Cu(111) and  $\text{Ni}_2\text{Cu}(111)$ . The intervening barriers between the  $\eta 2\text{NbNt}$  and  $\text{N}_2^* + \text{O}^*$  states are small ( $\leq 0.23$  eV). Irrespective of these low kinetic barriers, Cu(111) is still expected to be prone to releasing  $\text{N}_2\text{O}^*$  to the gas phase given the generally weak  $\text{N}_2\text{O}^*\text{-Cu}(111)$  interaction (Fig. 3(A)). The same is not true for  $\text{Ni}_2\text{Cu}(111)$  where the  $\text{N}_2\text{O}^*$  desorption energy is in the range of 0.65–0.74 eV, while the kinetic barriers that lead to  $\text{N}_2^* + \text{O}^*$  are between 0.06 eV and 0.23 eV (Fig. 3(C)). Given the similar energetics between the pathway of Fig. 3 and the “conventional” one, we conclude that both of them need to be considered in the reaction mechanism of the NO + CO reaction. Importantly, the existence of alternative  $\text{N}_2\text{O}^*$  decomposition paths may provide an explanation of the high selectivity to  $\text{N}_2$  exhibited by dilute Cu-based alloys.<sup>33</sup>

### 3.4. $\text{N}_2\text{O}$ formation and activation on Cu-based surfaces through the formation of $(\text{NO})_2^*$

Thus far, the formation of nitrous oxide was assumed to proceed through the coupling of  $\text{NO}^*$  and  $\text{N}^*$  species (Fig. 2 and 3).  $\text{NO}^*$  is of course the product of the molecular adsorption of gas-phase nitric oxide. On the other hand, the existence of  $\text{N}^*$  species implies prior scission of the N–O bond. In general, low-index coinage metal surfaces exhibit large kinetic barriers for the direct dissociation of  $\text{NO}^*$  ( $E_a = 1.57$  eV for Cu (111) and (100), and  $E_a > 2.5$  eV for Ag and Au (111) and (100) surfaces),<sup>4</sup> thereby being ineffective at activating the N–O







**Fig. 3** A second reaction path for the decomposition of  $N_2O^*$  on (A) Cu(111); (B) Ni/Cu(111) SAA and (C)  $Ni_2Cu(111)$ . State (1) corresponds to a  $\eta_2NbNt$  structure in all panels. The  $\eta_2-(N_i\{fcc\}, O\{top\})$  structure is state (2) and state (3) in panels (A) and (C), respectively. The zero level corresponds to infinitely separated (and thus non-interacting)  $N_2O$  molecule and clean slab. States without any labelling are transition states. Side views of the different states are shown in the ESI.† Ni, Cu, O and N atoms are shown in purple, orange, red and blue, respectively.

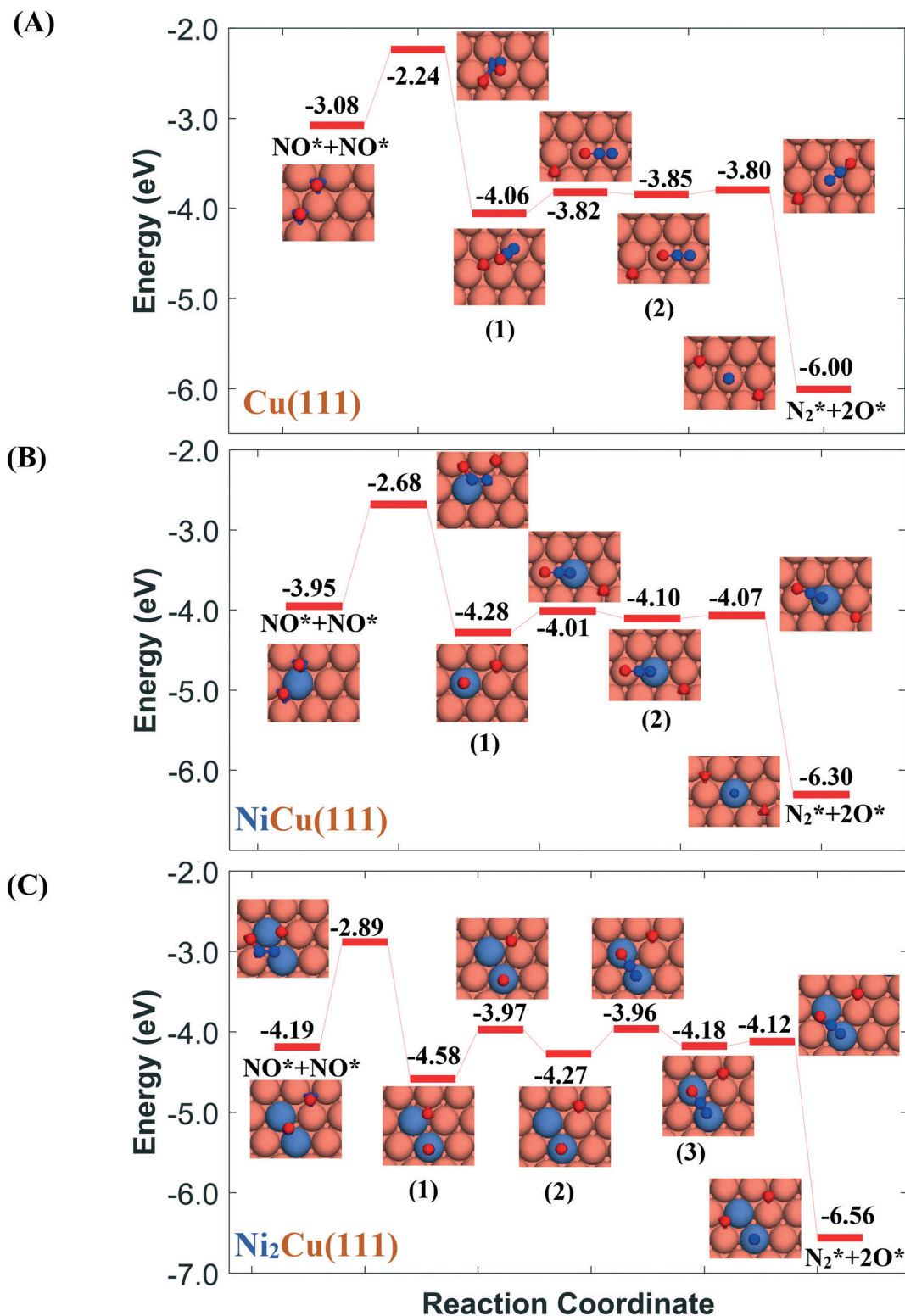
bond of  $NO^*$ . Yet, they are known to be active for the reduction of NO, which is mainly converted to  $N_2O$ . The activity of coinage metal surfaces is ascribed to the formation of  $NO^*$  dimer species (*i.e.*  $(NO)_2^*$ ) whose N–O bonds are more easily activated than those of monomeric  $NO^*$ .<sup>33,54,77–79</sup> This species is formed owing to vdW interactions between neighbouring  $NO^*$  species,<sup>80</sup> and may be observed even at relatively low  $NO^*$  coverages over Cu(111).<sup>43</sup> On the contrary, our calculations indicate that  $NO^*$  is adsorbed as a monomer on Rh(111) and this is corroborated by near edge X-ray absorption fine structure spectroscopy.<sup>81</sup>

The most energetically favoured adsorption structure of  $NO^*$  on Cu(111) is an N-down geometry where the N–O bond axis is perpendicular to the surface, and N is above an fcc hollow site ( $E_{ads}(NO) = -1.55$  eV).<sup>4</sup> A stable NO dimer is formed when two  $NO^*$  species are adsorbed on adjacent fcc sites ( $NO^* + NO^*$  state in Fig. 4(A)). We note that in the relaxed geometry of this state, the O atoms of the neighbouring nitric oxide adspecies are slightly tilted towards each other (Fig. 4(A)). The thermodynamic stability of this configuration has been confirmed by other DFT studies, as well as in scanning

tunnelling microscopy experiments.<sup>43,80</sup> The two neighbouring  $NO^*$  species can be converted to  $N_2O^*$  (with an  $\eta_1$  structure) and  $O^*$  (see state (1) in Fig. 4(A)). This is happening *via* a transition state where one of the two  $NO^*$  adsorbates bends down to the Cu(111) surface, while the other is slightly lifted (Fig. 4(A)). Once  $\eta_1 N_2O^*$  is formed, its decomposition occurs in the same way as in Fig. 2(A), namely through the formation of the  $\eta_2NtOt$  structure. We note that the structure of the  $(NO)_2^*$  transition state, and the computed barrier for the scission of the N–O bond *via* the  $(NO)_2^*$  precursor ( $E_a = 0.84$  eV) are in excellent agreement with the DFT calculations by Bogicevic and Hass ( $E_a = 0.82$  eV),<sup>54</sup> thereby furnishing further evidence for the reliability of our calculations.

We continue by investigating the same reaction pathway over the Ni/Cu(111) SAA and  $Ni_2Cu(111)$  surfaces. Our calculations show that the formation of  $N_2O^*$  *via* the dimerisation route is indeed possible over small Ni clusters. In contrast to Cu(111), on these dilute alloys  $(NO)_2^*$  adopts a flat geometry parallel to the surfaces in the transition state, and the computed kinetic barriers are 1.27 eV and 1.30 eV for Ni/Cu(111) SAA and  $Ni_2Cu(111)$ ,





**Fig. 4** Reaction pathway for the formation and decomposition of  $\text{N}_2\text{O}^*$  via  $(\text{NO})_2^*$  for (A) Cu(111); (B) Ni/Cu(111) SAA; and (C)  $\text{Ni}_2\text{Cu}(111)$ . The zero level corresponds to two non-interacting gas-phase NO molecules and a clean slab. States without any labelling are transition states. Side views of the different states are shown in the ESI.† Ni, Cu, O and N atoms are shown in purple, orange, red and blue, respectively.

respectively (Fig. 4(A) and (B)). These values are higher than the computed barrier for Cu(111) – ( $E_a = 0.84$  eV), and this may be attributed to the extra energy cost required for

bending down both  $\text{NO}^*$  species. Nevertheless, they are lower than or equal to the corresponding kinetic barriers for the direct dissociation of  $\text{NO}^*$  ( $E_a = 1.47$  eV and 1.30 eV



for Ni/Cu(111) SAA and Ni<sub>2</sub>Cu(111), respectively).<sup>4</sup> Therefore, the formation and decomposition of N<sub>2</sub>O\* through dimerisation is another pathway that should be included in the reaction mechanism of the NO + CO reaction over the Cu-based alloy surfaces.

To elucidate the effect of the Ni cluster size to the formation rate of  $\eta 1$  N<sub>2</sub>O\* and O\* via the (NO)<sub>2</sub>\* intermediate, we perform additional calculations for the Ni<sub>3</sub>-Cu(111) surface (Fig. S5†). On this surface, we compute  $E_a = 1.77$  eV and  $E_a = 1.37$  eV for the splitting of the N–O bond via dimerisation (Fig. S5†) and via the direct NO\* dissociation,<sup>4</sup> respectively. Additionally, we note that on Ni dimers and trimers the formed  $\eta 1$  N<sub>2</sub>O\* can be transformed to the  $\eta 2\text{NtOt}$  (state (3) in Fig. 4(C) for Ni<sub>2</sub>Cu), and decompose to N<sub>2</sub>\* + 2O\* only after O\* spillover to Cu(111). The barrier for O\* diffusion from a mixed hollow site to a Cu hollow site over Ni<sub>2</sub>Cu(111) (from state (1) to state (2) in Fig. 4(C)) is 0.61 eV. Therefore, this extra energy cost in conjunction with the large kinetic barrier for the scission of the N–O bond of (NO)<sub>2</sub>\* render the decomposition of N<sub>2</sub>O\* through the dimerisation pathway less likely on Ni clusters with more than two Ni atoms.

### 3.5. The microkinetics of the NO + CO reaction over Ni/Cu dilute alloys

Using the computed energetics for the decomposition of N<sub>2</sub>O\* in conjunction with previous results for the formation of N<sub>2</sub>\*, CO\* oxidation and NO\* decomposition over Ni/Cu surfaces,<sup>4</sup> we parameterise a microkinetic model for the NO + CO reaction. Our studies include one site type for Cu(111) and Rh(111) surfaces, and two site types for the bimetallic surfaces (see section 2). The goal is a preliminary assessment of the catalytic performance of the Ni/Cu dilute alloys and a comparison to Cu(111) and Rh(111). Accordingly, the microkinetic simulations are performed in the absence of adsorbate–adsorbate interactions,<sup>82–85</sup> whose effects on the coverage profiles, and consequently on the catalytic performance of the Cu-based surfaces may be important (this is part of ongoing research). Regarding the bimetallic surfaces, we assume that Ni\* species (single atoms or dimers) can be occupied by one adspecies (e.g. CO\*), which can react with another adspecies on a Cu site (e.g. O\*) and form a product on the Ni site (e.g. CO<sub>2</sub>\*). Such events are treated as reactions that take place on the dopant site, and follow the energetics computed over the Ni site of the Ni/Cu surfaces. On the contrary, the Cu(111) energetics are used if the reaction involves two adspecies that are both on Cu sites (Table S3†). Despite their simplicity, such microkinetic models are capable of capturing the salient features of experimental trends,<sup>86</sup> providing mechanistic insights,<sup>87</sup> and aiding in the identification of the active site during catalysis.<sup>88,89</sup>

The NO + CO reaction mechanism is composed of 16 reversible reaction steps, shown in Table 2 along with their forward and reverse barriers. For all simulations the total pressure is set to 16.0 Torr with  $P_{\text{NO}} = P_{\text{CO}} = 8.0$  Torr, thereby

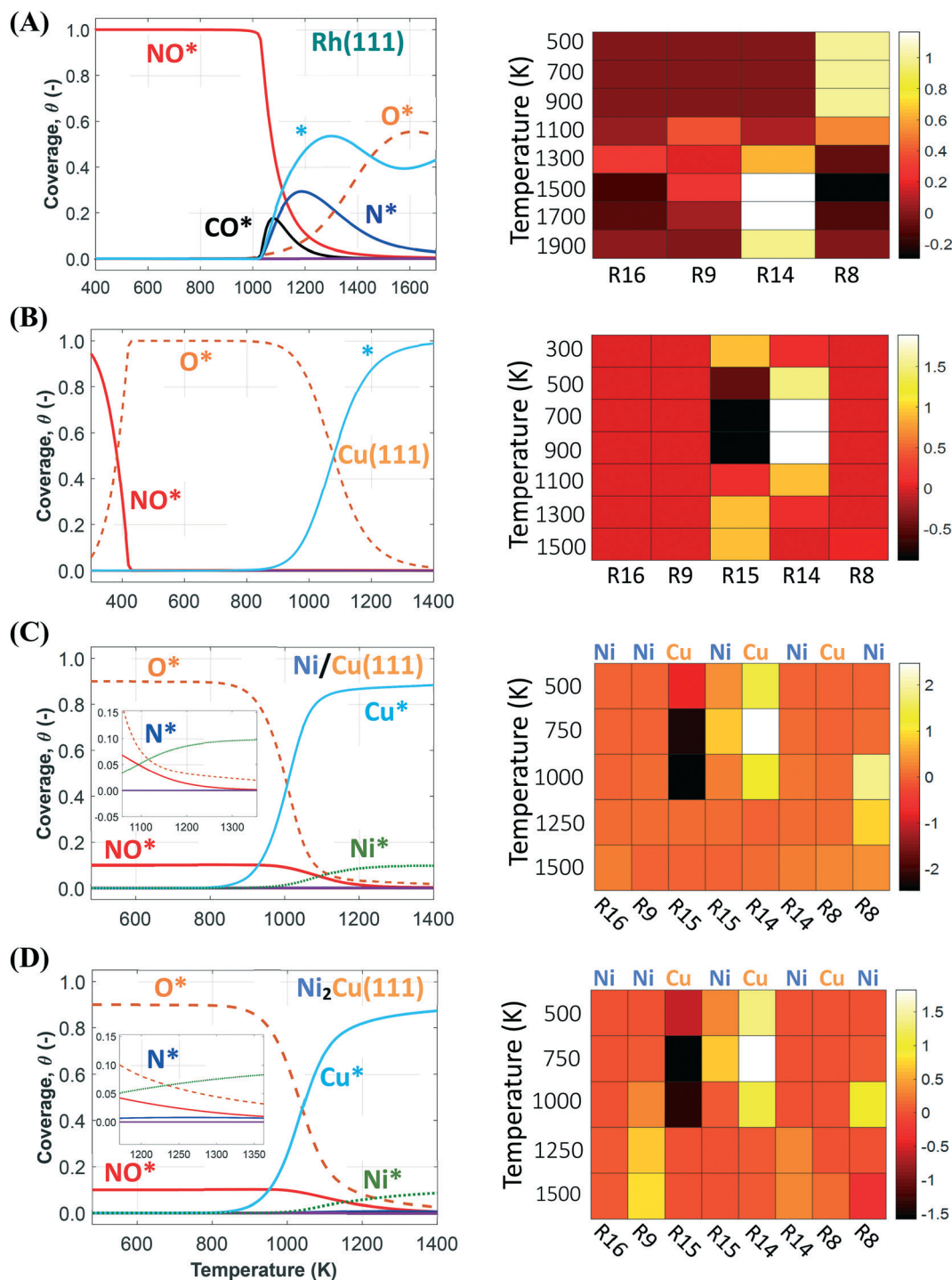
replicating the experimental conditions of Belton and co-workers.<sup>13</sup> At this point, we note that the associative desorption of O<sub>2</sub> and the formation of NO<sub>2</sub>\* are reactions through which O\* may be removed from the surface and they could be included in the microkinetic model. However, both of them exhibit very high kinetic barriers, and on this basis are excluded from the reaction mechanism. For example, the computed barrier for the O<sub>2</sub>\* association reaction on Cu(111) is 2.10 eV, while the barrier for the reverse process is just 0.16 eV (see section 7 in the ESI†); these values are in reasonable agreement with former DFT calculations.<sup>90</sup> Along the same lines, we find that the dissociation of NO<sub>2</sub>\* to NO\* + O\* is significantly more facile than its formation and its desorption (see section 7 in the ESI†).

We first simulate the NO + CO reaction on Rh(111). The total coverages of the surface species and the DRC analysis for this surface are shown in Fig. 5(A). The coverage profiles reveal that the catalyst surface is saturated with NO\* species up to temperatures of 1000 K. Under these conditions, the high surface coverage gives rise to steric hindrance effects, which prevent the dissociation of NO\*. This behaviour has been reported in the experimental work of Herman *et al.*, and is in qualitative agreement with the fact that Rh(111) is catalytically active only at temperatures higher than 625 K.<sup>13</sup> Moreover, our model predicts that surface sites are freed up by NO adspecies only at  $T > 1000$  K; this high “ $T$  threshold” can be attributed to (1) the absence of the repulsive NO\*–NO\* interactions in our microkinetics (see Fig. S4 in the ESI†); and (2) the very strong NO\*–Rh(111) interaction predicted by the optB86b-vdW functional. In particular, NO\*–NO\* interactions may contribute to the reduction of the surface coverage, and in turn, this will generate free sites whereon the dissociation of NO\* can happen at lower temperatures than those predicted by our model.<sup>91,92</sup> Regarding the second point, we find that the most stable adsorption site for NO\* on Rh(111) is hcp, in line with previous computational and experimental works.<sup>5,93,94</sup> However, we compute  $E_{\text{ads}}(\text{NO}) = -2.85$  eV, which is larger than the PW91 values of Mavrikakis *et al.*<sup>94</sup> ( $-2.39$  eV –  $2 \times 2$  cell) and of González *et al.*<sup>93</sup> ( $-2.62$  eV –  $3 \times 3$  cell). Unfortunately, at coverages of 0.11 ML, like in our DFT calculations, accurate experimental measurement of  $E_{\text{ads}}(\text{NO})$  is challenging because of the tendency of NO\* to dissociate on Rh(111).<sup>94</sup> The reduction of the NO\* surface coverage gives rise to the formation of N\* and O\* at  $T > 1000$  K. The accumulation of N\* species in the temperature range of 1000–1200 K, is associated with the inefficiency of Rh(111) in forming  $\eta 2\text{NbNt}$  N<sub>2</sub>O\* (R9,  $E_a = 1.50$  eV) and N<sub>2</sub>\* (R16,  $E_a = 1.85$  eV) – (Table 2). Both reaction steps are rate-limiting with a positive DRC coefficient ( $0.19 \leq X_{\text{DRC,R9}} \leq 0.30$ ) between 1100 K and 1300 K (Fig. 5(A)). Along the same lines, the build-up of O\* is ascribed to the moderate activation barrier for the CO\* oxidation reaction ( $E_a = 1.17$  eV – R14 in Table 2), which is the only reaction that exhibits a reasonable activation barrier for the removal of O\* from the surface.

The corresponding coverage profiles and DRC analysis for Cu(111) are displayed in Fig. 5(B). Cu(111) exhibits rather







**Fig. 5** Total coverage (eqn (3)) profiles and DRC coefficients ( $X_{RC}$ ) for the NO + CO reaction steps for (A) Rh(111); (B) Cu(111); (C) Ni/Cu(111) SAA; and (D) Ni<sub>2</sub>Cu(111).  $X_{RC}$  values are presented at various temperatures by means of heatmaps; the site whereon the reaction occurs is shown on the top of the heatmaps for the bimetallic surfaces.

different behaviour than Rh(111). In particular, at  $T < 350$  K all surface sites are occupied by NO\*, but at  $T > 350$  K there is a sharp increase in the coverage of the O\* species. This sharp transition is attributed to the activation of the N–O bond *via* the NO\* dimerisation reaction ( $E_a = 0.84$  eV) – (R15 in Table 2), which converts  $2\text{NO}^*$  to O\* and  $\eta 1 \text{N}_2\text{O}^*$ . The

catalyst surface remains fully covered by O\* within the temperature range of 420–900 K. Accordingly, our DRC analysis shows that under these conditions, the oxidation of CO\* controls the reaction rate, and that the NO\* dimerisation is an inhibiting step as it adds more O\* onto the surface (Fig. 5(B)).



The last two coverage profiles shown in Fig. 5 (panels (C) and (D)) are those for the Ni/Cu alloy surfaces. These surfaces contain a total of 10 000 sites, out of which 9000 are Cu sites (Cu\*) and 1000 are Ni sites (Ni\*). The coverage profiles are very similar in both cases, and indicate that Cu\* sites are covered with O\* up to ca. 900 K (similar to Cu(111)), while Ni\* sites are poisoned by NO\*. A disparity between the two surfaces is seen between 1000 K and 1500 K, where we observe a small build-up of N\* over Ni<sub>2</sub>Cu(111) only (Fig. 5(C) and (D)). The presence of N\* on the latter surface is indicative of the direct NO\* dissociation (R8,  $E_a = 1.30$  eV – Table 2), which happens to a smaller extent on the SAA surface (R8,  $E_a = 1.47$  eV – Table 2). Markedly, the N\* accumulation remains at low levels thanks to the efficiency of Ni<sub>2</sub>Cu(111) in forming N<sub>2</sub>\* and η<sup>2</sup>NbNt N<sub>2</sub>O\* (Table 2). The latter can either decompose to N<sub>2</sub>\* + O\* (R10, R11, R12 and R13) or desorb (R5).

Next, we examine the activity and selectivity to N<sub>2</sub> of the four surfaces. The latter metric is computed as

$$S_{N_2/N_2O} = \frac{R_{N_2,net}}{R_{N_2,net} + R_{N_2O,net}}, \quad (16)$$

$R_{N_2,net}$  and  $R_{N_2O,net}$  are the net reaction rates for N<sub>2</sub> and N<sub>2</sub>O, respectively (see eqn (13) and (14)).

Fig. 6 displays the activity plots for the studied surfaces, where the catalytic rate is provided by the computed turnover frequency (TOF) at various temperatures. The observed trend for Rh(111) (Fig. 6(A)) can be rationalised based on the corresponding coverage plot (Fig. 5(A)). As seen in Fig. 6(A), the activity of Rh(111) is low below 950 K owing to the high NO\* coverage, which hinders the direct NO\* dissociation (Fig. 5(A)). On the contrary, for  $T > 950$  K there is an increase in the catalytic activity. Initially the rate of N<sub>2</sub>O production is greater than that of N<sub>2</sub>, and only at  $T > 1200$  K the two production rates become equal (Fig. 6(A)).

Similarly to Rh(111), the catalytic activity of Cu(111) can be explained from the coverage profile plot in Fig. 5(B). For this surface, low (*i.e.* 300–500 K) and high (*i.e.* 500–1400 K) temperatures can be discussed separately. Between 300 K and 420 K, we observe that the catalytic activity increases steadily (see Fig. S11 in the ESI†), and the surface transitions from a

NO\*-rich phase to an O\*-rich phase. As discussed earlier, this transition is associated with the dimerisation reaction (R15 in Table 2), which consumes NO\*, releases N<sub>2</sub>O and yields O\*. At ca. 420 K, there is a sharp reduction in the catalytic activity (Fig. S11†), and this is the result of the poisoning of Cu(111) by O\* species. The surface remains in the poisoned state for temperatures up to ca. 700 K, where the removal of O\* species happens efficiently and the dimerisation reaction begins to take place again at considerable rates (see Fig. 6(B) and the heatmap in Fig. 5(B)). Finally, for  $T > 1000$  K there is a decrease in the catalytic activity (Fig. 6(B)) because under these conditions, the gaseous state of the reactants is preferred over adsorption on the catalytic surface. Throughout the investigated temperature range, the production rate of N<sub>2</sub>O is far greater than the production rate of N<sub>2</sub>, and this is attributed to the inability of Cu(111) to directly dissociate NO\* as well as to the weak binding of the η<sup>1</sup> N<sub>2</sub>O\* produced by the dimerisation reaction.

On the other hand, enhanced catalytic activity can be achieved when Ni\* species are present in Cu(111) (Fig. 6(C) and (D)). Remarkably, the production rate of N<sub>2</sub> is considerably larger on Ni/Cu(111) SAA than on Cu(111) and even more so on Ni<sub>2</sub>Cu(111), where the N<sub>2</sub> and N<sub>2</sub>O production rates become equal beyond 1000 K.

Given the importance of  $S_{N_2/N_2O}$ , this section concludes with an investigation on this metric, followed by suggestions for further improvements in this regard. Regarding Rh(111), our microkinetic model predicts that the main nitrogen-containing product from Rh(111) at  $T < 1000$  K is N<sub>2</sub>O, whilst the production of N<sub>2</sub> exhibits a substantial increase beyond 1100 K (Fig. 7(A)). The latter temperature corresponds to the point where the surface sites are freed up (Fig. 5(A)), and the dissociation of NO\* is enabled. Notably, this trend is qualitatively in line with the reactor experiments of Peden *et al.*<sup>12</sup> on Rh(111). The experiments showed that Rh(111) exhibits poor selectivity to N<sub>2</sub> for reaction temperatures up to 700 K; yet, the authors observed a sharp increase in  $S_{N_2/N_2O}$  at temperatures higher than that. One should expect that closer quantitative agreement can be achieved by accounting for coverage effects, which will tend to

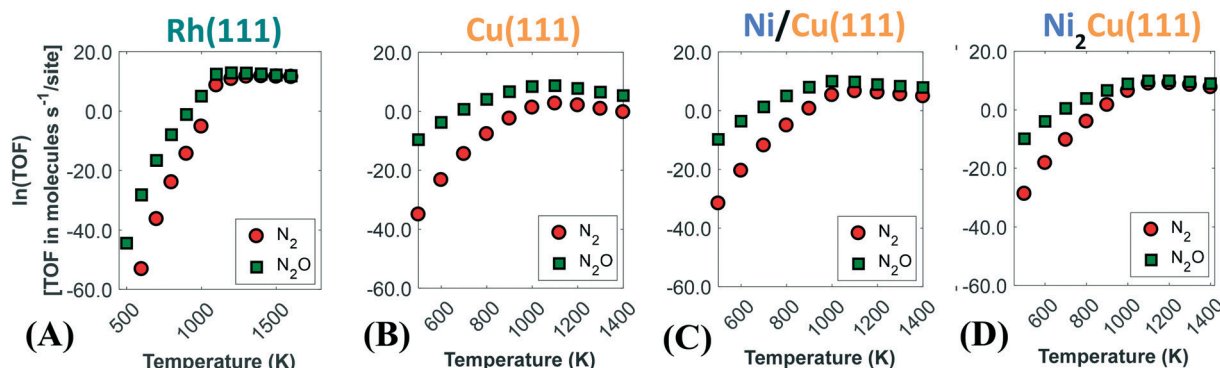


Fig. 6 Rates of production of nitrogen-containing products for (A) Rh(111); (B) Cu(111); (C) Ni/Cu(111) SAA; and (D) Ni<sub>2</sub>Cu(111).



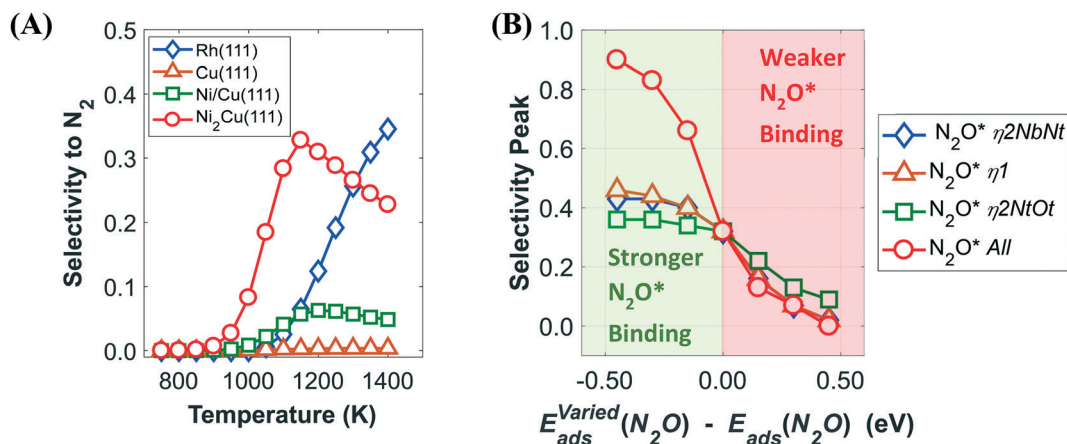


Fig. 7 (A) Selectivity to N<sub>2</sub> for Cu(111), Rh(111) and the Ni/Cu alloys. (B) Maximum of the N<sub>2</sub> selectivity peak at various N<sub>2</sub>O\* adsorption energies. Values on the right correspond to smaller N<sub>2</sub>O\* binding strength on Ni\* than the DFT-computed (red shade); values on the left correspond to larger N<sub>2</sub>O\* binding strength on Ni\* than the DFT-computed (green shade). In the simulations of panel (B) only the desorption energy of N<sub>2</sub>O\* was varied, whilst all the other kinetic barriers were kept fixed at their DFT-computed values.

decrease the surface coverage at  $T < 1000$  K (see Fig. S4†), thereby freeing up sites and shifting the profiles of Fig. 5 to lower temperatures.

The same analysis for Cu(111) reveals that this surface is indeed susceptible to the formation of N<sub>2</sub>O (Fig. 7(A)). We find that the main way of forming N<sub>2</sub>O\* (in the  $\eta$ 1 structure) on Cu(111) is *via* the formation of the (NO)<sub>2</sub> intermediate followed by N–O activation (R15). This is in line with molecular beam/infrared spectroscopy studies on other Cu low-index surfaces.<sup>77</sup> The  $\eta$ 1 N<sub>2</sub>O\* can go through one of the following paths: (1) desorb directly ( $E_a = 0.21$  eV); (2) transform to  $\eta$ 2NtOt N<sub>2</sub>O\* ( $E_a = 0.06$  eV) and either desorb ( $E_a = 0.20$  eV) or dissociate to N<sub>2</sub>\* + O\* ( $E_a = 0.05$  eV); (3) transform to  $\eta$ 2NbNt N<sub>2</sub>O\* ( $E_a = 0.56$  eV) and desorb spontaneously. Therefore, N<sub>2</sub>O\* can easily undergo transformations over Cu(111), but in every new state there is a high probability for desorption, thereby explaining the poor N<sub>2</sub> selectivity of this surface.

Interestingly, the catalytic behaviour Ni/Cu(111) SAA and Ni<sub>2</sub>Cu(111) appears to be more similar to Rh(111), which is well established for the NO + CO reaction, than to Cu(111), which is the host metal (Fig. 7(A)). In more precise terms, it is observed that on each of the dilute alloy surfaces the selectivity to N<sub>2</sub> remains low at  $T < 900$  K but increases sharply at higher temperatures similarly to Rh(111).  $S_{N_2/N_2O}$  for both Ni/Cu(111) SAA and Ni<sub>2</sub>Cu(111) exhibits an interesting behaviour by which it first increases for  $T > 900$  K and then decreases at 1200 K.

To shed light on this behaviour, we have carried out additional microkinetic simulations for Ni<sub>2</sub>Cu(111) where the activation barrier of one of the following events on Ni\* is assigned a very large value (e.g. 2.5 eV): (1) NO\* direct dissociation (R8); (2) N<sub>2</sub>\* formation (R16); (3) NO\* dimerisation (R15); and (4)  $\eta$ 2NbNt N<sub>2</sub>O\* formation (R9). In doing so, we record how the selectivity peak responds to the obstruction of the aforementioned events (see section 9 in the ESI†). We determine that the selectivity spike in the two

bimetallic surfaces is associated with the direct dissociation of NO\* and the formation of  $\eta$ 2NbNt N<sub>2</sub>O\*, which could subsequently decompose to N<sub>2</sub>\* + O\* (see section 9 in the ESI†). Therefore, it is the ability of Ni/Cu alloys to form and process  $\eta$ 2NbNt N<sub>2</sub>O\* that gives rise to the selectivity peak in Fig. 7(A). The selectivity to N<sub>2</sub> enters a downturn because at  $T > 1200$  K, there is a rise in the N<sub>2</sub>O\* desorption rate. On the other hand, the formation of N<sub>2</sub> on Rh(111) is solely relying on the direct dissociation of NO\* and such a selectivity spike is not observed (Fig. 7(A)).

Accordingly, the higher intensity of the N<sub>2</sub> selectivity peak on Ni<sub>2</sub>Cu(111) than on Ni/Cu(111) SAA can be explained by: (1) the higher concentration of N\* species on Ni<sub>2</sub>Cu(111) owing to its better ability to dissociate NO\* as compared to Ni/Cu(111) SAA (see Table 2 and Fig. 5(D)); (2) the generally stronger interaction between N<sub>2</sub>O\* and Ni<sub>2</sub>Cu(111) than that between N<sub>2</sub>O\* and Ni/Cu(111) SAA (Table 2), noting that strong interaction will favour the decomposition of N<sub>2</sub>O\* over its desorption.

Moreover, we explore the effect of the N<sub>2</sub>O\* binding strength on the height of the selectivity peak on Ni<sub>2</sub>Cu(111) by performing a sensitivity analysis with respect to  $E_{ads}(N_2O)$  – (Fig. 7(B)). Remarkably, the adsorption energy of N<sub>2</sub>O\* appears to have a great impact upon the N<sub>2</sub> selectivity at 1100–200 K (Fig. 7(B)). For example, shifting the adsorption energy of all N<sub>2</sub>O\* adsorption structures to more negative values by 0.15 eV and 0.30 eV (*i.e.* stronger binding) results to an increase in the maximum of the peak by 0.31 (from 0.33 to 0.67) and 0.52 (from 0.33 to 0.85), respectively. We conjecture that binding strengths of this magnitude may be provided by sites on more open low-index surfaces (*e.g.* (100) and (110)) but also on stepped surfaces, and if this is true, the presence of such sites will contribute dramatically to the N<sub>2</sub> selectivity at low temperatures. Therefore, this result underscores the potential of well-engineered dilute Ni/Cu alloys for the NO + CO reaction and creates motivation for further investigations.





Finally, given the importance of  $E_{\text{ads}}(\text{N}_2\text{O})$  we have computed the binding energy of  $\text{N}_2\text{O}^*$  using other vdW functionals, including optPBE-vdW, BEEF-vdW,<sup>95</sup> and the Tkatchenko–Scheffler method (DFT-TS) – (see Table S4 in the ESI†). The latter method is similar to the DFT-D2 method of Grimme,<sup>96</sup> with the difference that the dispersion coefficients and the damping function in the dispersion correction are dependent on the charge density.<sup>97</sup> These additional calculations highlight that significant variations in the predicted  $E_{\text{ads}}(\text{N}_2\text{O})$  should be expected when treating vdW interactions based on different approaches,<sup>98</sup> thereby influencing the predictions of *ab initio* microkinetic and kinetic Monte Carlo models (see section 11 in the ESI†).

## 4. Concluding remarks

By means of DFT calculations, we performed a thorough investigation of the formation and decomposition of  $\text{N}_2\text{O}^*$  over Rh(111), Cu(111), a Ni/Cu(111) SAA surface and a Ni<sub>2</sub>-Cu(111) surface, where Ni atoms form dimer clusters. The DFT-derived energetics, in conjunction with results from our previous work,<sup>4</sup> were then used to parameterise a microkinetic model for the NO + CO reaction.

Our DFT calculations showed that the presence of a small amount of Ni over Cu(111) strengthens significantly the interaction between  $\text{N}_2\text{O}^*$  and the catalyst surface. This enhanced interaction is desirable because it prevents the desorption of  $\text{N}_2\text{O}^*$ , thereby benefiting the selectivity to  $\text{N}_2$  during the NO + CO reaction. Regarding the decomposition of  $\text{N}_2\text{O}^*$ , we explored three competing reaction paths. In the first pathway the decomposition products (*i.e.*  $\text{NO}^* + \text{O}^*$  and  $\text{N}_2^* + \text{O}^*$ ) are connected through the  $\eta_1$  adsorption structure of  $\text{N}_2\text{O}^*$ . In the second, the same products are connected through another  $\text{N}_2\text{O}^*$  adsorption structure (*i.e.*  $\eta_2\text{-(N}_t\{\text{fcc}\}, \text{O}\{\text{top}\})$ ), and the third involves the formation of an  $(\text{NO})_2^*$  intermediate. These paths exhibit comparable energetics and therefore merit consideration when modelling the kinetics of the NO + CO reaction. We also demonstrated that the selectivity of the Ni/Cu dilute alloy surfaces can be manipulated by tuning the size of the Ni cluster; generally, the formation of  $\text{NO}^*$  and atomic nitrogen is kinetically favoured over “large clusters” (*e.g.* trimers), whereas small clusters (*i.e.* dimers) and single atoms promote the dissociation of  $\text{N}_2\text{O}^*$  to  $\text{N}_2^*$  and atomic oxygen.

Finally, the performance of the Ni/Cu dilute alloy surfaces was assessed by means of microkinetic simulations for the NO + CO reaction. Our studies highlighted the potential of Ni<sub>2</sub>Cu(111), which showed considerably improved catalytic performance as compared to Cu(111) and comparable performance to the best transition metal for the reduction of NO (*i.e.* Rh(111)). Future work could focus on the effect of adsorbate–adsorbate interactions on the reaction kinetics of the NO + CO reaction,<sup>99–101</sup> and explore the behaviour of other facets of the Ni<sub>2</sub>Cu catalyst in an effort to quantify potential structure-sensitivity effects.

## Conflicts of interest

There are no conflicts of interest to declare.

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