Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The effect of the surface coverage on N_2, NO and N_2O formation over Pt(111)

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Supplementary material: This supplementary material provides the configurations of the double-species adsorption configurations that were calculated in this study, providing the energy difference between the most stable configurations presented in the main manuscript and those configurations that were found less energetically prefered (Figures S1 to Figure S5). In addition, we present the configuration of the transition states of all reaction paths together with the imaginary frequencies as a function of the surface coverage (Figures S6 to Figures S9).

Figure S1. Configurations of the double-species co-adsorption at 0.06 and 0.125 ML. Configurations with a ΔE = 0 corresponds to the most stable configuration, presented in Figure 2 of the main manuscript. Configurations with a ΔE different to zero correspond to less stable co-adsorption. The energy difference with the most stable configuration is reported as ΔE in kJ mol^{-1}. The colour coding corresponds to Blue: nitrogen atom, Red: oxygen atom and Gray: platinum atom.

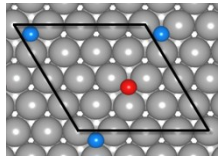
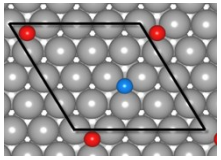
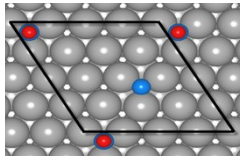
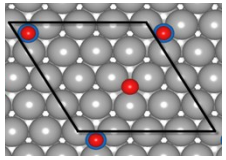
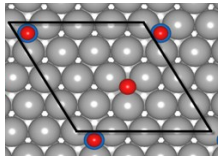
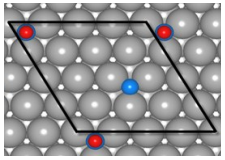
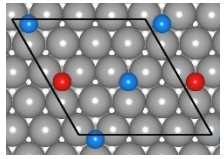
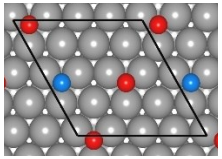
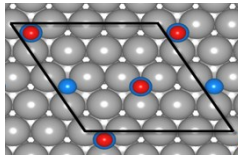
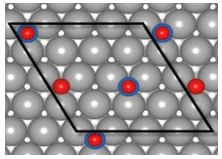
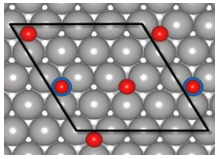
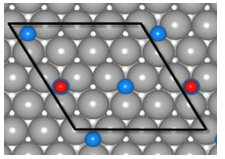
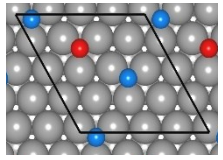
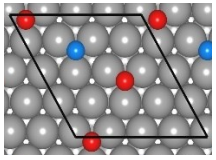
Configurations	**O^*–(N^*)**	**N^*–(O^*)**	**N^*–(NO^*)**	**O^*–(NO^*)**	**NO^*–(O*)**	**NO*–(N*)**	θ
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.06 ML
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.125 ML
Conf2	 ΔE = 21	 ΔE = 15	---	---	---	---	

Figure S2. Configurations of the double-species co-adsorption at 0.25 ML. Configurations with a ΔE = 0 corresponds to the most stable configuration, presented in Figure 2 of the main manuscript. Configurations with a ΔE different to zero correspond to a less stable co-adsorption. The energy difference with the most stable configuration is reported as ΔE in kJ mol^{-1}.

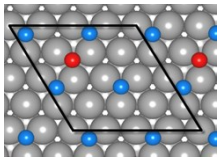
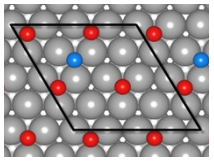
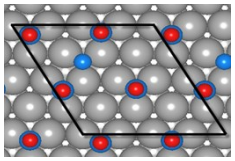
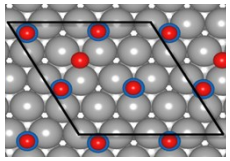
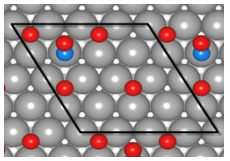
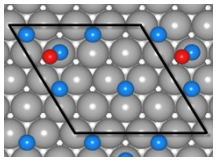
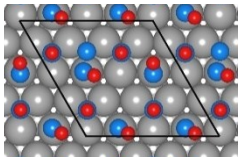
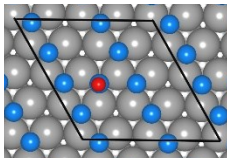
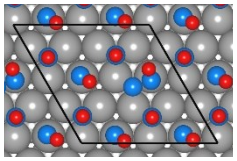
Configurations	O^*–(N^*)	N^*–(O^*)	N^*–(NO^*)	O^*–(NO^*)	NO^*–(O*)	**NO*–(N*)**	θ
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.25 ML
Conf2	---	---	 ΔE = 43	---		 ΔE = 11	
Conf3	---	---	 ΔE = 45	---			

Figure S3. Configurations of the double-species co-adsorption at 0.375 ML. Configurations with a ΔE = 0 corresponds to the most stable configuration, presented in Figure 2 of the main manuscript. Configurations with a ΔE different to zero correspond to a less stable co-adsorption. The energy difference with the most stable configuration is reported as ΔE in kJ mol^{-1}.

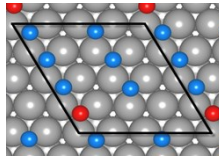
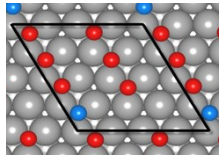
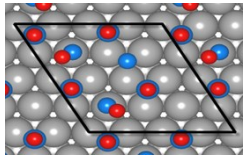
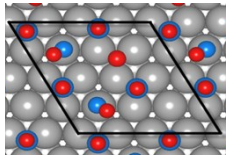
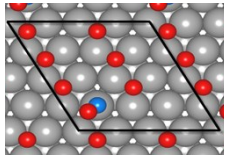
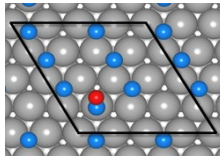
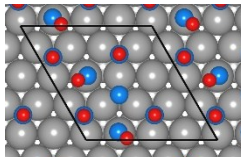
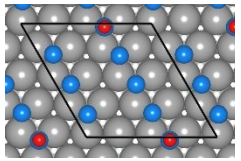
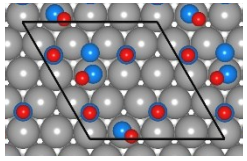
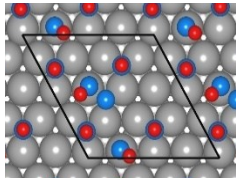
Configurations	O^*–(N^*)	N^*–(O^*)	N^*–(NO^*)	O^*–(NO^*)	NO^*–(O*)	**NO*–(N*)**	θ
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.375 ML
Conf2	--- ---	--- ---	 ΔE = 29	--- ---		 ΔE = 36	
Conf3	--- ---	--- ---	 ΔE = 78	--- ---			
Conf4	--- ---	--- ---	 ΔE = 79	--- ---			

Figure S4. Configurations of the double-species co-adsorption at 0.44 ML. Configurations with a ΔE = 0 corresponds to the most stable configuration, presented in Figure 2 of the main manuscript. Configurations with a ΔE different to zero correspond to a less stable co-adsorption. The energy difference with the most stable configuration is reported as ΔE in kJ mol^{-1}.

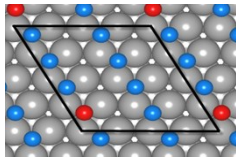
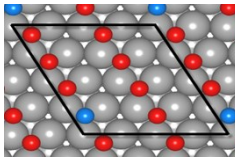
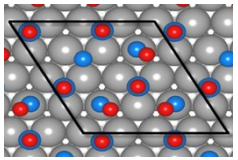
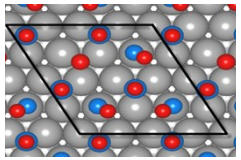
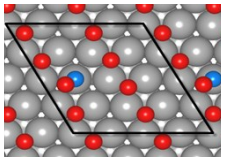
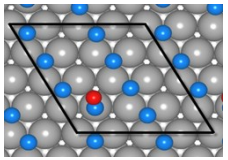
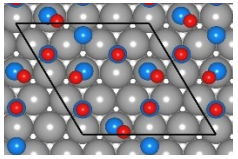
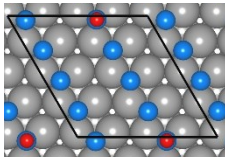
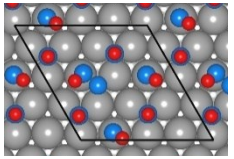
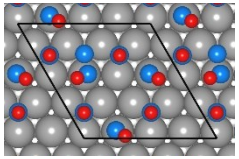
Configurations	O^*–(N^*)	N^*–(O^*)	N^*–(NO^*)	O^*–(NO^*)	NO^*–(O*)	**NO*–(N*)**	θ
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.44 ML
Conf2	---	---	 ΔE=12	---	---	 ΔE = 31	
Conf3	---	---	 ΔE=52	---	---	---	
Conf4	---	---	 ΔE=54	---	---	---	

Figure S5. Configurations of the double-species co-adsorption at 0.44 ML. Configurations with a ΔE = 0 corresponds to the most stable configuration, presented in Figure 2 of the main manuscript. Configurations with a ΔE different to zero correspond to a less stable co-adsorption. The energy difference with the most stable configuration is reported as ΔE in kJ mol^{-1}.

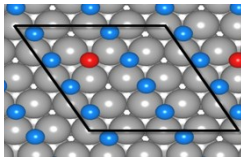
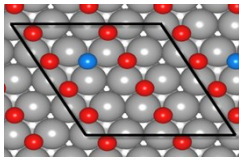
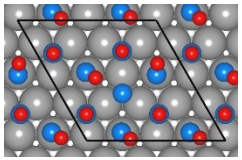
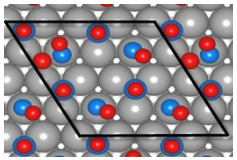
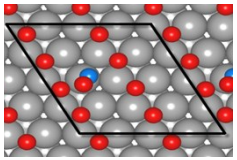
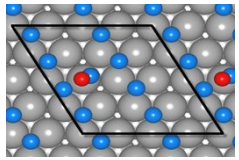
Configurations	O^*–(N^*)	N^*–(O^*)	N^*–(NO^*)	O^*–(NO^*)	NO^*–(O^*)	**NO*–(N*)**	θ
Conf1	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	 ΔE = 0	0.5 ML
Conf2	--- --- ---	--- --- ---	ΔE = 43	--- --- ---		ΔE = 11	
Conf3	--- --- ---	--- --- ---	ΔE = 45	--- --- ---			

Figure S6. Schematic representation of the transition states with their respective imaginary frequencies for NO formation at 0.06,0.125, 0.25, 0.31 and 0.5 ML θ_{O^*}. ΔE_a (in kJ mol^{-1}) is referenced to the most stable initial configuration. Gray: platinum atom blue: nitrogen atom and red: oxygen atom. Bond distances are in Å.

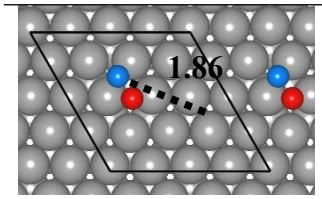
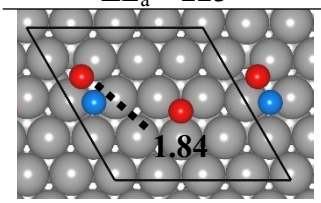
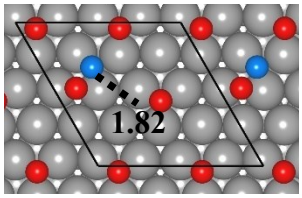
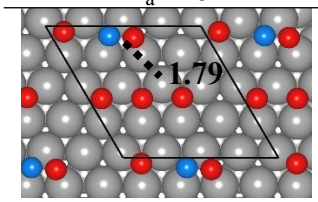
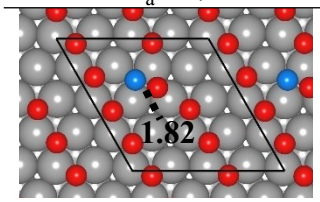
TS	Frequency (cm^{-1})	θ_{O^*}
 $\Delta E_a = 223$	401*i*	0.06 ML
 $\Delta E_a = 222$	418*i*	0.125 ML
 $\Delta E_a = 182$	448*i*	0.25 ML
 $\Delta E_a = 172$	448*i*	0.31 ML
 $\Delta E_a = 120$	526*i*	0.5 ML

Figure S7. Schematic representation of the transition states with their respective imaginary frequencies for N_2(g) formation at 0.125,0.19, 0.25, 0.38 and 0.5 ML θ_{N^*}. ΔE_a (in kJ mol^{-1}) is referenced to the most stable initial configuration. Gray: platinum atom blue: nitrogen atom and red: oxygen atom. Bond distances are in Å.

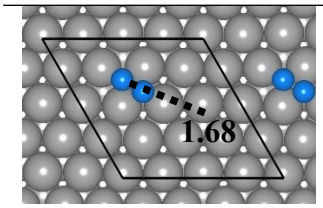
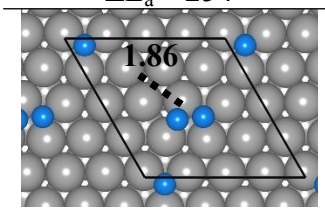
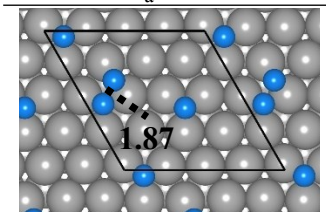
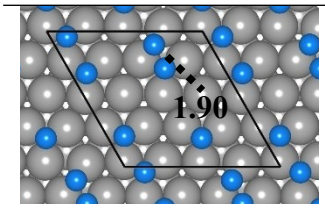
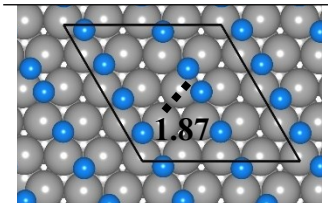
TS	Frequency (cm^{-1})	θ_{O^*}
 ΔE_a = 254	634*i*	0.125 ML
 ΔE_a = 225	476*i*	0.19 ML
 ΔE_a =224	459*i*	0.25 ML
 ΔE_a =155	448*i*	0.375 ML
 ΔE_a =113	523*i*	0.5 ML

Figure S8. Schematic representation of the transition states with their respective imaginary frequencies for N_2O(g) formation at 0.06,0.125, 0.25, 0.31 and 0.5 ML θ_{N^*}. ΔE_a (in kJ mol^{-1}) is referenced to the most stable initial configuration. Gray: platinum atom blue: nitrogen atom and red: oxygen atom. Bond distances are in Å.

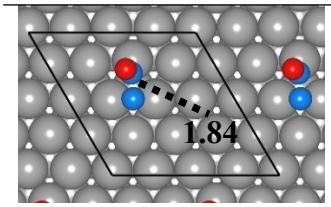
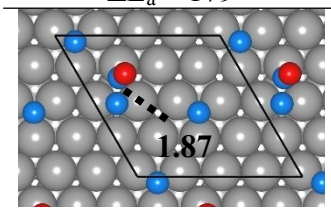
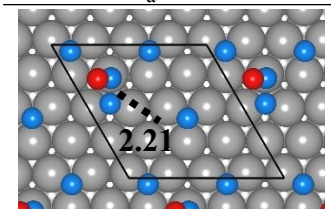
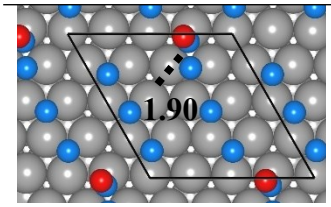
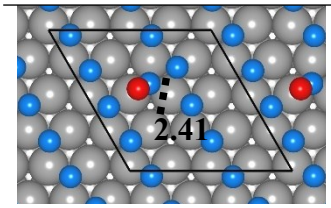
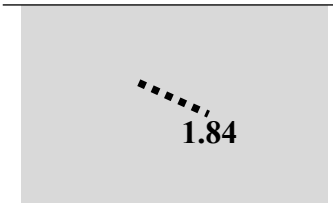
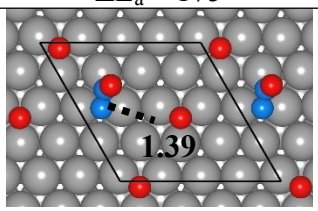
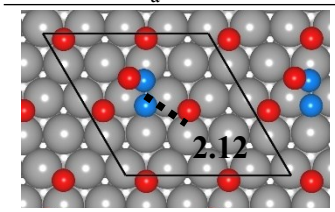
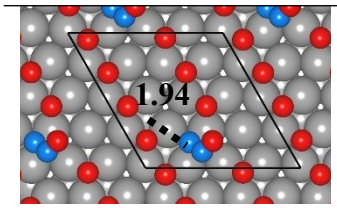
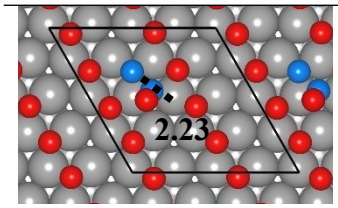
TS	Frequency (cm^{-1})	θ_{O^*}
 ΔE_a = 179	273*i*	0.06 ML
 ΔE_a = 168	330*i*	0.19 ML
 ΔE_a =125	166*i*	0.25 ML
 ΔE_a =56	330*i*	0.375 ML
 ΔE_a =32	248*i*	0.5 ML

Figure S9. Schematic representation of the transition states with their respective imaginary frequencies for N_2O(g) formation at 0,0.125, 0.25, 0.44 and 0.5 ML θ_{O^*}. ΔE_a (in kJ mol^{-1}) is referenced to the most stable initial configuration. Gray: platinum atom blue: nitrogen atom and red: oxygen atom. Bond distances are in Å.

TS	Frequency (cm^{-1})	θ_{O^*}
 ΔE_a = 175	273*i*	0 ML
 ΔE_a = 175	175*i*	0.125 ML
 ΔE_a =145	166*i*	0.25 ML
 ΔE_a =113	118*i*	0.44 ML
 ΔE_a =105	248*i*	0.5 ML