

**NO reduction over noble metal catalysts:
Origin of the high N₂O selectivity in the presence
of metallic states**

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Motivation

NO reduction in the presence of O₂



Catalysts design

1. Platinum group metals, Ru, Rh, Ir, Pt

O₂ poisoning at high temperatures and oxidative conditions

2. Noble metals, Ag and Au

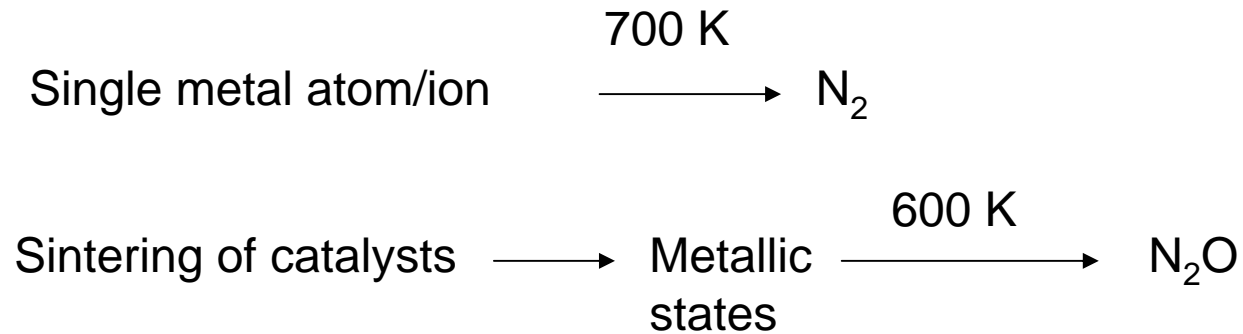
😊 Resistant to O₂

Reactivity of Ag-based catalysts

Single crystal

Ag{111} ~80 K, convert NO to N₂O through a (NO)₂ dimer intermediate

Real catalyst, Ag/Al₂O₃



Why ?

Speculative Mechanisms

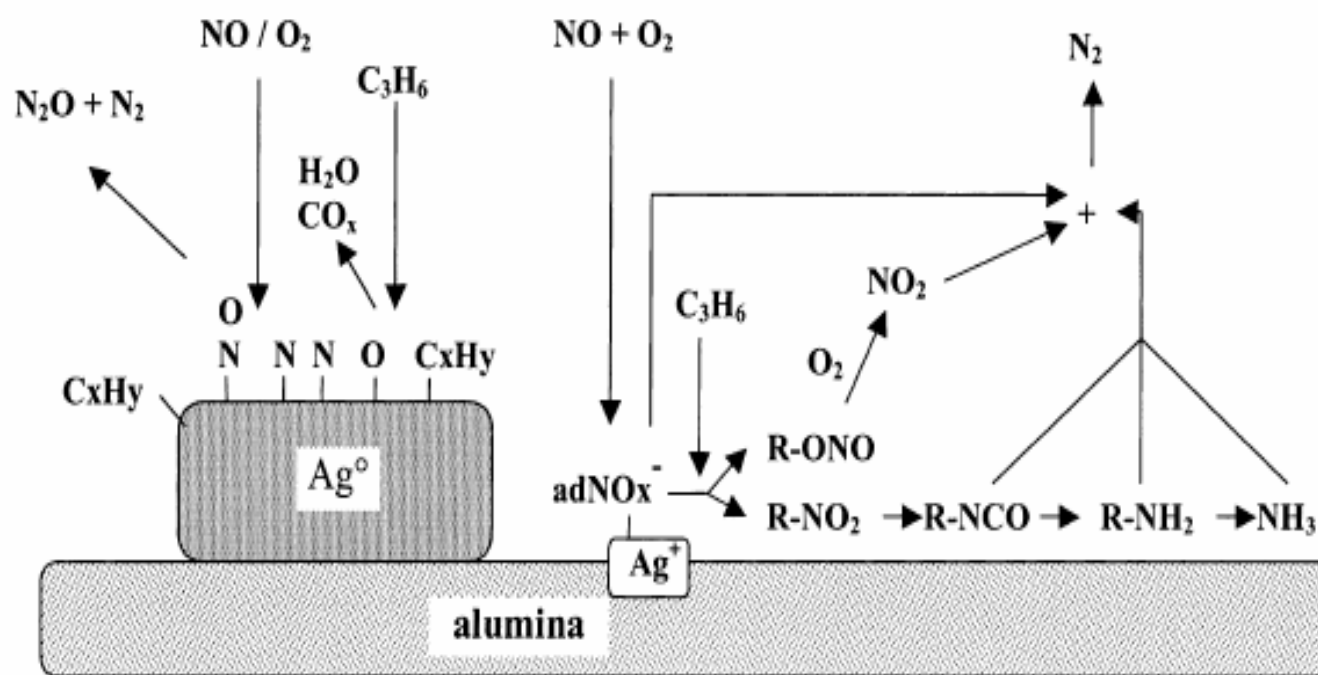


Fig. 6. The different roles of Ag during the C₃H₆-SCR over Ag/γ-Al₂O₃: large Ag⁰ particles catalyse the decomposition-reduction of NO, whereas Ag⁺ species favours the oxidation of NO to ad-NO_x species which subsequently react through the intermediacy of organo-nitrogen compounds. Adapted from [14].

Methodology

1. Density functional theory

2. Plane wave basis set

3. Supercell approach

CASTEP

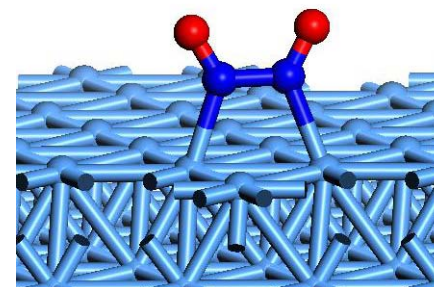
4. Ultrasoft pseudopotentials

5. Constrained minimisation technique

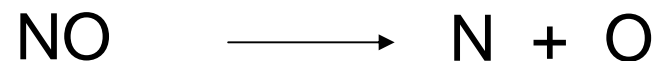
Searching Transition State

Adsorption of NO monomer and dimer on different Ag surfaces

	CN (Ag)	E_{ad} (Monomer)	E_{ad} (Dimer)
Ag{111}	9	0.36 (1/4 ML) 0.15 (1/9 ML)	1.12 (1/9 ML)
Ag{211}	6	0.61 (1/6 ML)	1.57 (1/6 ML)
Ag-adatom	1	0.57 (1/9 ML)	
Ag ₁₂	6	0.47	1.20
Ag ₁₂ ²⁺	6	0.71	1.35



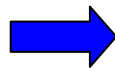
Is NO dissociation possible ?



$$E_{\text{bond}} = 6.67 \text{ eV}$$

	E_a (eV)	ΔH (eV)
Ag{111}	3.11	+2.47
Ag{211}	2.70	+2.20

N adsorption energy
is particularly low



1.50 eV on Ag{111}

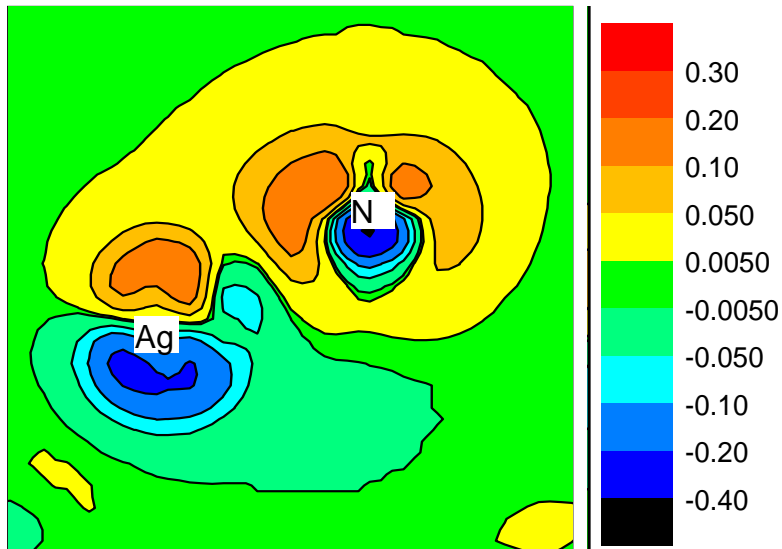
O: 2.70 eV

1.56 eV on Ag₁₂

1.51 eV on Ag₁₂²⁺

Why is the binding energy of N atom on Ag so low?

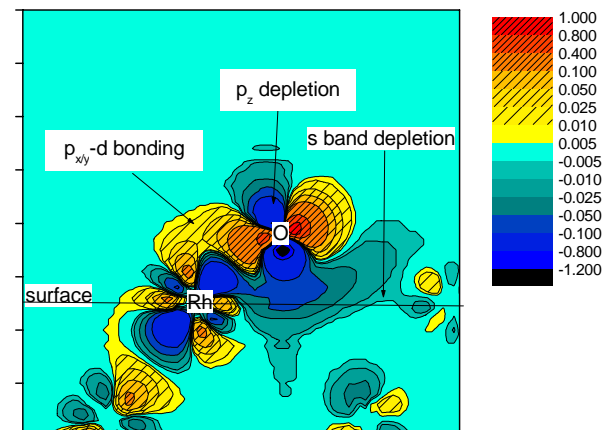
Charge density difference plot showing the N-Ag bonding plane



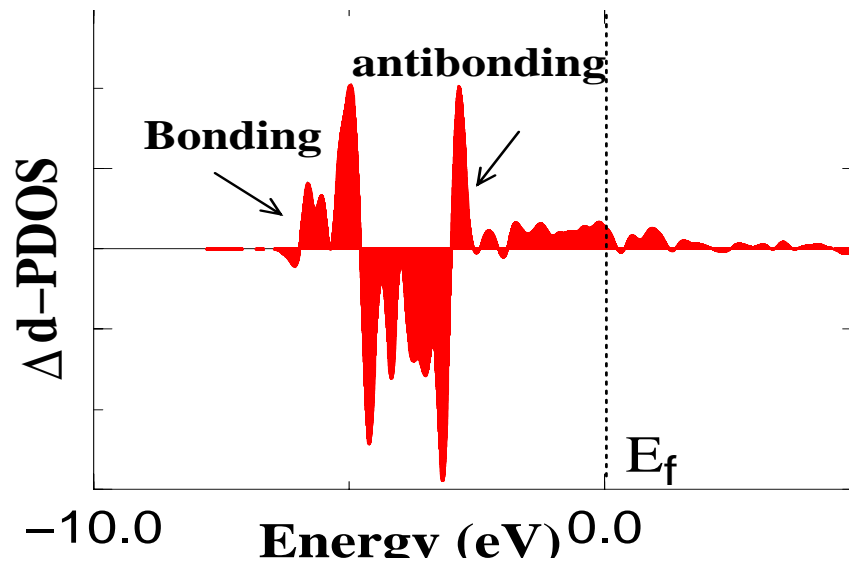
Charge accumulation towards N atom

Mainly Ionic bonding

Weak p - d mixing



Ag *d*-states energy change before and after the adsorption of N atom



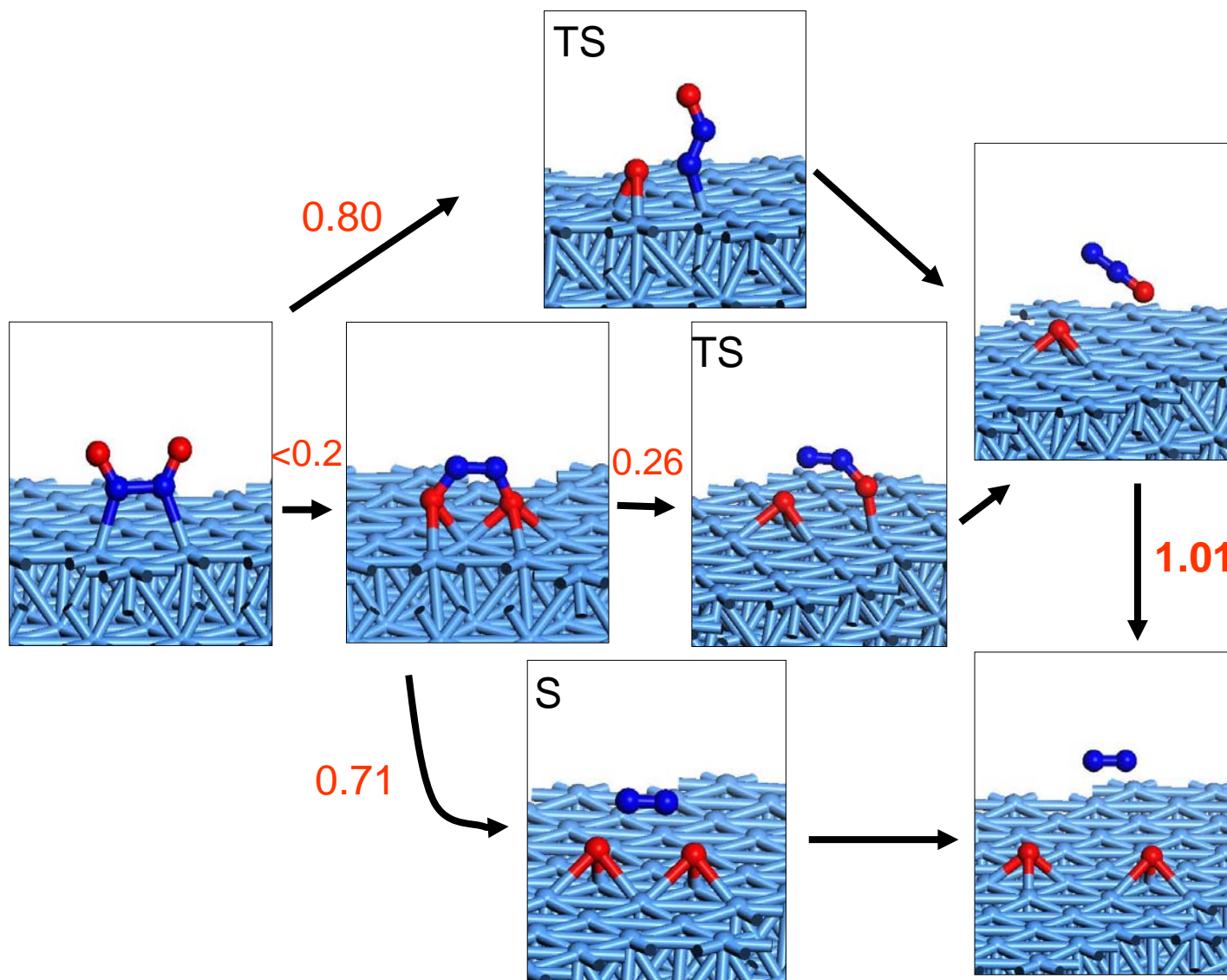
Pauli repulsion

d-band energy cost **+0.26 eV**

-3.94 eV for N adsorption
on the transition metal Ir

Ag-based catalysts have no good covalent bonding sites for N atoms.

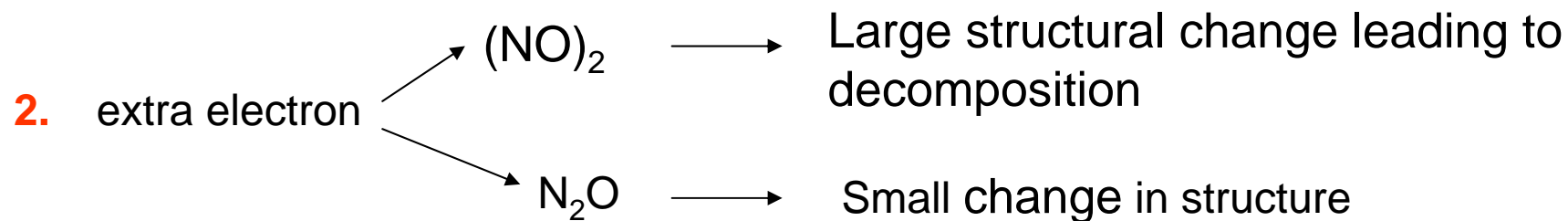
Pathways initiated from the $(\text{NO})_2$ dimer



Explain the reactivity

	(NO) ₂	NO	N ₂ O
E _{ad} (eV)	1.12	0.15	0.02
Mulliken charge (e)	-0.56	-0.37	-0.04
Electron affinity (eV)	-1.50	-0.50	+0.15

1. Higher bonding ability of (NO)₂ on Ag is due to its higher EA



Conclusions

NO dissociation is unlikely on Ag-based catalysts because of the preference of N atoms to the covalent bonding

$(\text{NO})_2$ decomposition to N_2O is facile intrinsically; The further decomposition of N_2O is kinetically hindered.

The located dimer pathway can explain the experimental observation for the high N_2O selectivity in the presence of Ag metallic state