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Exploring dynamic catalytic processes for low-temperature ammonia synthesis on Ru-supported nanoparticles

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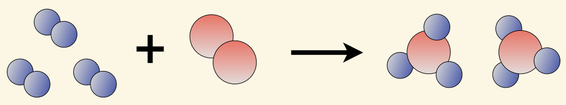
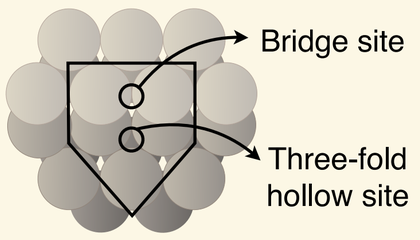
BACKGROUND

$3H_{2\,(g)} + N_{2\,(g)} \longrightarrow 2NH_{3\,(g)}$

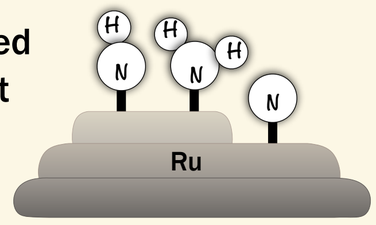


High amounts of NH_3 can be produced at low temperature in presence of a highly active catalytic material (1)

- Ru nanoparticles with stepped surfaces can catalyze the reaction (2)
- B_5 site: the most active site for N_2 dissociation (2)



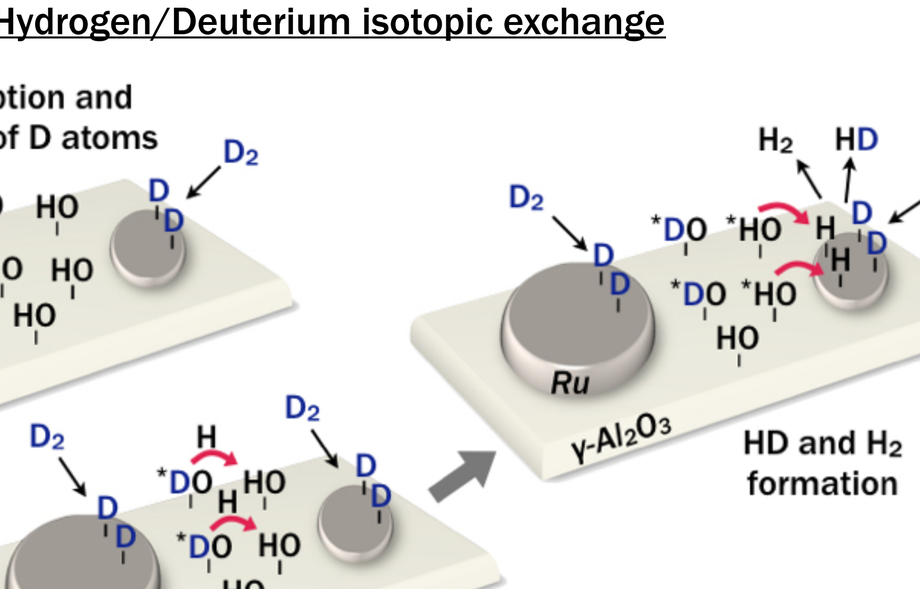
- Low temperatures: NH_x intermediates are strongly attached to Ru stepped surfaces (3)
  - B_5 sites are blocked
  - Local environment of B_5 sites is modified (4)



CATALYSTS SYNTHESIS

$Ru/\gamma\text{-}Al_2O_3$ (Different Ru loadings; Single catalysts and mixtures)

WET IMPREGNATION	COLLOIDAL METHOD	W/O MICROEMULSION



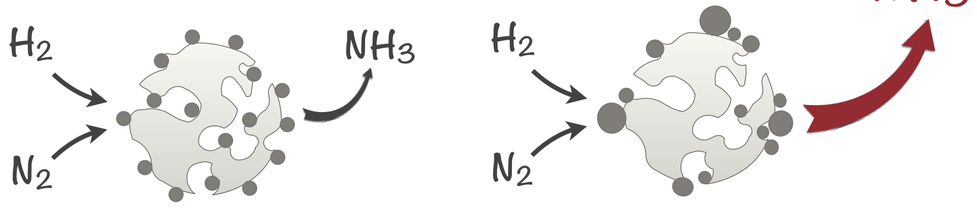
Ru supported nanoparticles with different mean size, distribution of sizes and surface arrangement

OBJECTIVE

To elucidate the processes occurring at low temperature, upon interaction of H_2 and N_2 with a catalytic surface containing Ru nanoparticles.

MAIN FINDINGS

1. Synergy in the catalytic activity between Ru nanoparticles of different sizes



✗ Mono-sized, well-separated Ru nanoparticles

✓ Poly-sized Ru nanoparticles in close proximity

2. Hydrogen diffusion on alumina via exchange with OH groups

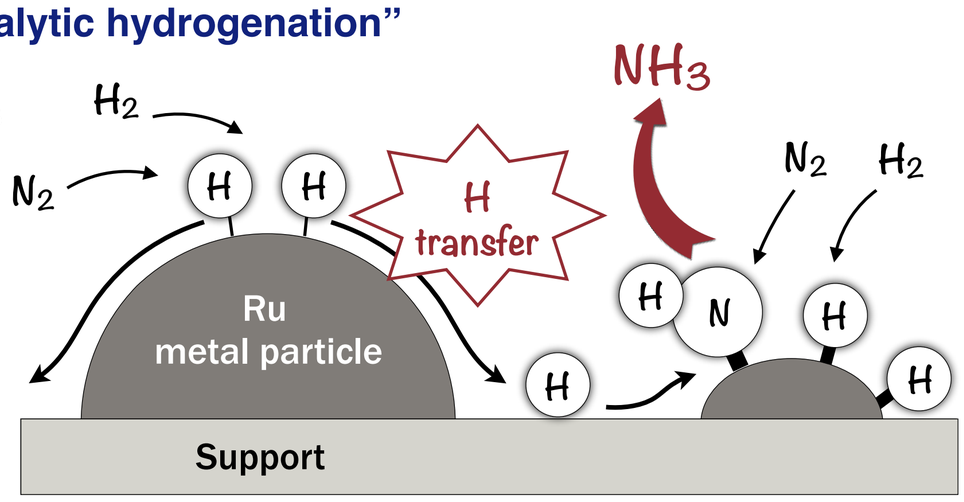
Hydrogen/Deuterium isotopic exchange

3. Small vs. large Ru supported nanoparticles

Small Ru nanoparticles	Large Ru nanoparticles
Higher number of B_5 sites	Low number of B_5 sites
Strong adsorption of hydrogen on Ru particles	Faster hydrogen adsorption/desorption
Lower diffusivity of H atoms on the support	Higher diffusivity of H atoms on the support
Very slow hydrogenation of NH_x intermediates	NH_x intermediates are more rapidly hydrogenated

4. "Dynamic mechanism of low-temperature catalytic hydrogenation"

- Transfer of H atoms from large to small nanoparticles
- Promotion of hydrogenation of NH_x strongly attached to small particles
- Promotion of reaction rate by:
  (i) direct release of B_5 sites
  (ii) regulation of the local environment and properties of B_5 sites



Catalyst requirements

- ✓ Support that allows diffusion of H atoms
- ✓ Metal nanoparticles in close proximity and with an adequate size distribution

CONCLUDING REMARKS

1. The size distribution and proximity of supported metal particles can strongly influence their catalytic performance
2. Dynamic processes can arise at the catalyst surface, involving transfer of reactive species and a continuous modification of the properties of metal particles
3. These processes can lead to catalytic cooperation (or inhibition) between neighbouring metal particles
4. The study of dynamic surface process with significant implications on the kinetics and reaction pathways can be crucial to:
   - ✓ perform catalytic processes with lower energy consumption and higher selectivity
   - ✓ formulate of more accurate kinetic models

Literature cited

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