Cluster as a model for chemistry in the interstellar environment

Protoplanetary disk

Mineral particles and ions

Cluster ions consisting of Mg, Fe, Al, Si, O

Fischer-Tropsch reaction

\[(2n+1)H_2 + n\text{CO} \xrightarrow{\text{Fe, Ni, Al}_2\text{O}_3, \text{MgO, Si}} C_nH_{2n+2} + nH_2O\]

Reaction of mineral clusters with CO, H_2O, H_2 and N_2...
Experiment

$$\text{Si}_n\text{O}_m^- + \text{H}_2\text{O} \rightarrow ?$$

**Diagram Description:**
- **Ion deflector**
- **CO at 300 K**
- **Reaction cell**
- **Q-mass spectrometer** (Identification of products)
- **Ion detector** (Observation of reaction products)
- **Quadrupole mass filter** (Size selection)
- **Cooling cell**
- **O$_2$/He gas**
- **Cluster ion source** ($\text{Mg}/\text{Si}_n\text{O}_m^-$)
- **Cooling cell**
- **lq. N$_2$**
- **sputtering targets (Si)**
Reaction of SiₙOₙ₋ with CO: n = 5

- High reactivity toward CO
- CO adducts

\[ P_{CO} = 7.4 \times 10^{-1} \text{ Pa} \]
\[ E_{col} \text{ with CO was 0.8 eV} \]

- Si₅O₉⁻ (reactant)
- Si₅O₁₀⁻ (reactant)
- Si₅O₁₁⁻ (reactant)
- Si₅O₁₂⁻ (reactant)

No reaction products

Small peaks

CO adducts

Generation of CO₂
Rate constants of the adsorption reaction

Rate constants were high for $m \geq 2n + 1$
Adsorption sites of a CO molecule on Si\textsubscript{n}O\textsubscript{m}−: \(n = 3\)

**\(\text{Si}_3\text{O}_m^-\)**

- four-fold coordination forming a SiO\textsubscript{4} tetrahedron
- planar three-fold coordination
- triangular-pyramidal three-fold coordination

**3a** Si\textsubscript{3}O\textsubscript{5}− (non reactive)

**3b** Si\textsubscript{3}O\textsubscript{6}− (non reactive)

**3c** Si\textsubscript{3}O\textsubscript{7}− (reactive)

Local charges of O atoms are typically −1.2\(e\)−−1.3\(e\). (NBO analysis)

- adsorption site of CO:
  - A dangling O atom of the pair appearing in Si\textsubscript{3}O\textsubscript{2n+1}−

- Adsorption energy:
  - \(3a'\) S\textsubscript{3}O\textsubscript{5}(CO)− (\(D_0 = 0.31\) \(eV\))
  - \(3b'\) S\textsubscript{3}O\textsubscript{6}(CO)− (\(D_0 = 0.45\) \(eV\))
  - \(3c'\) S\textsubscript{3}O\textsubscript{7}(CO)− (\(D_0 = 1.12\) \(eV\))

\(m \geq 2n + 1\)

(Optimized using the Gaussian09 package, B3LYP/aug-cc-pVDZ)
Site selectivity: Location of SOMO

\[ \text{Si}_3\text{O}_m^- \]

3a \text{Si}_3\text{O}_5^- 

\[ 3a' \text{S}_3\text{O}_5(\text{CO})^- \]

3b \text{Si}_3\text{O}_6^- 

\[ 3b' \text{S}_3\text{O}_6(\text{CO})^- \]

3c \text{Si}_3\text{O}_7^- 

\[ 3c' \text{S}_3\text{O}_7(\text{CO})^- \]

Pair of dangling \text{O} atoms

Isosurfaces of SOMOs

\[ m \geq 2n + 1 \]

(Optimized using the Gaussian09 package, B3LYP/aug-cc-pVDZ)
**Summary**

✨ Reaction of $\text{Si}_n\text{O}_m^-$ with a CO molecule

✨ **A pair of dangling O atoms** on four-fold coordinated Si atoms, which appears in $\text{Si}_n\text{O}_{2n+1}^-$, plays a key role for CO adsorption

✨ **The site selectivity** is governed by the location of SOMO on $\text{Si}_n\text{O}_m^-$