

DISTINCT FORMULATIONS AND SELECTIVE TUNING OF PREVAILING SPECIES IN $\text{ReO}_x/\text{ZrO}_2$ CATALYSTS: AN IN SITU MOLECULAR SPECTROSCOPIC VISTA

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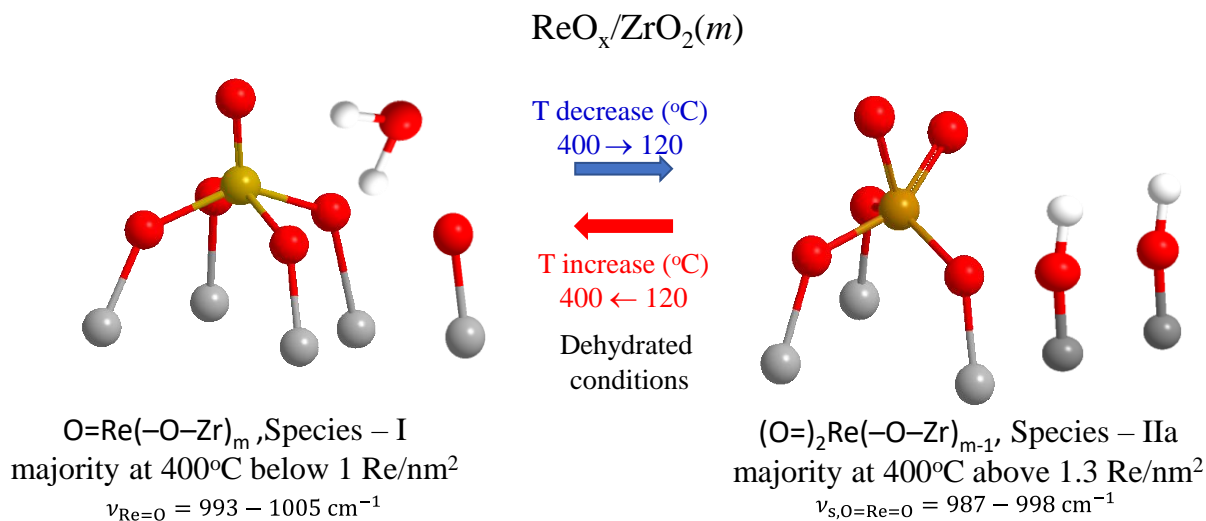
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ABSTRACT

In situ Raman and FTIR spectra complemented by in situ Raman/¹⁸O isotope labelling are exploited for deciphering the structural properties and configurations of the $(\text{ReO}_x)_n$ phase dispersed on monoclinic ZrO_2 at temperatures of 120 – 400 °C under oxidative dehydration conditions and coverages in the range of 0.71 – 3.7 Re/nm^2 . The dispersed $(\text{ReO}_x)_n$ phase is heterogeneous, consisting of three distinct structural units: a) Species – I with mono-oxo termination $\text{O}=\text{Re}(-\text{O}-\text{Zr})_m$ ($\text{Re}=\text{O}$ mode at 993 – 1005 cm^{-1}); b) Species – IIa with di-oxo termination $(\text{O}=\text{O})_2\text{Re}(-\text{O}-\text{Zr})_{m-1}$ (symmetric stretching mode at 987 – 998 cm^{-1}); and c) Species – IIb with di-oxo termination $(\text{O}=\text{O})_2\text{Re}(-\text{O}-\text{Zr})_u$ (symmetric stretching mode at 982 – 991 cm^{-1}); all terminal stretching modes undergo blue shifts with increasing coverage. With increasing temperature, a reversible temperature-dependent Species – IIa \rightarrow Species – I transformation is evidenced (see Figure). At low coverages, below 1 Re/nm^2 , isolated species prevail; at 400 °C the mono-oxo $\text{O}=\text{Re}(-\text{O}-\text{Zr})_m$ Species – I is the majority species, the di-oxo Species – IIa occurs in significant proportion and di-oxo Species – IIb is in minority. At coverage $\geq 1.3 \text{ Re}/\text{nm}^2$, at 400°C the di-oxo Species – IIa prevails clearly over mono-oxo Species – I and. Below 80 °C and at a low coverage of 0.71 Re/nm^2 , the occurrence of a fourth structural unit, Species – III taking on a tri-oxo configuration (symmetric stretching mode at 974 cm^{-1}) is evidenced. All temperature-dependent structural and configurational transformations are fully reversible and interpreted by mechanisms at the molecular level. ^[1]



KEYWORDS: supported transition metal oxides, rhenia, molecular structure, Raman, FTIR

REFERENCES

[1] Andriopoulou C., Kentri Th., Boghosian S. (2024). *Dalton Trans*, 53, <https://doi.org/10.1039/D3DT04270G>.