**DISTINCT WVIOx CONFIGURATIONS DISPERSED ON TITANIA.   
TEMPERATURE AND COVERAGE EFFECTS.**

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**ABSTRACT**Titania supported tungsta constitute a class of materials widely used in environmental and industrial catalysis. To date, literature reports on the molecular structure of (WOx)n sites dispersed on TiO2 are far from being in consensus. Site configurations (i.e., mono-oxo vs di-oxo), wolfram coordination and aspects related to occurrence of multiple sites with distinct configurations remain open. Literature reports have often relied to one or two samples below monolayer coverage or to spectroscopic measurements after cooling the sample or to “fast” spectroscopic measurements, thereby suffering from one or more deficiencies.

Chart

Description automatically generatedIn the present work, all available tools of *in situ* molecular vibrational spectroscopy are deployed in the temperature range of 120 – 430oC. *In situ* Raman spectroscopy complemented by *in situ* FTIR in the overtone spectral region and *in situ* Raman/18O isotope exchange measurements have been applied for probing the heterogeneity of the molecular structural configurations of WVIOx dispersed on titania. Incipient wetness impregnation was utilized to synthesize supported WOx/TiO2 catalysts on two variations of TiO2 (P25 and anatase) at coverages up to the approximate monolayer (0.5 – 4.5 W/nm2). Moreover, results of neoteric Raman studies in sealed quartz cells under static equilibrium were exploited to cross-check the *in situ* findings, extended also in hydroxyl region of the spectra. Distinct WOx site configurations (“Species-I”, “Species-II” and Species-III”) were identified, the prevalence of which is ruled by temperature and coverage. A reversible temperature-dependent molecular level mechanism mediated by water molecules retained on the support is proposed to account for the “Species-II” ↔ Species-III” transformation.

Hence, the current study addresses open questions regarding the prevalence of particular molecular WOx structures deposited on titania and the heterogeneity of the dispersed WOx phase on TiO2.

**KEYWORDS:** tungsta/titania catalysts; dispersed phase configurations; in situ spectroscopy; temperature depen-dence; surface characteristics

**Figure.** Sequential*in situ* Raman and FTIR spectra obtained for 2.1 WOx/TiO2(P25) in order of decreasing temperatures. Evidence for occurrence of three distinct species [(I), (II) and (III)].