New Insights from LEIS about Anomalous Surface Compositions of Stoichiometric Mixed Oxide Compounds*

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Heterogeneous Catalysis

- **Catalysts accelerate chemical reactions and control relative activity of reaction pathways giving rise to enhanced selectivity**
- **Heterogeneous catalysis involves chemical reactions between gaseous or condensed molecules and solid surfaces of catalysts**
- **Molecules can not diffuse into bulk lattice of solid catalysts unless solids are porous (e.g., zeolites)**
- **Heterogeneous catalysis models for mixed oxides have traditionally assume that the catalyst surfaces are just truncations of the bulk lattice**

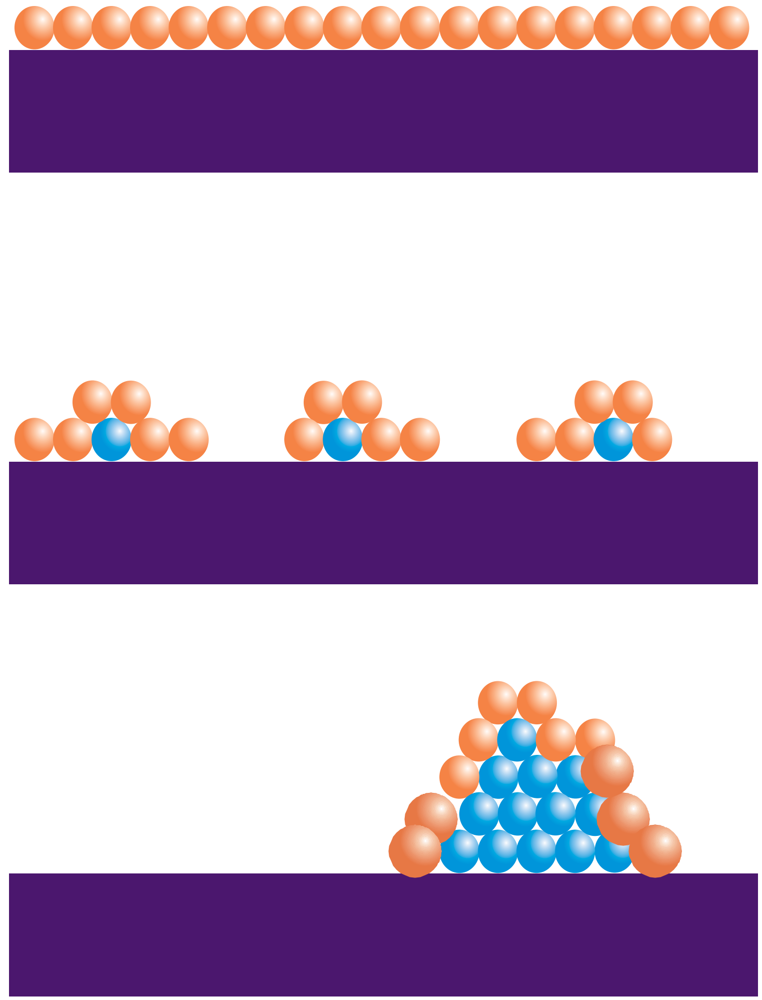
Modern Surface Analysis Techniques

X-ray Photoelectron Spectroscopy (XPS):
Provides composition and oxidation states,
BUT averaged over <u>10–20 atomic layers (1-3 nm)</u>

Low Energy Ion Scattering (LEIS) Spectroscopy:
Provides composition of <u>outermost surface layer</u>
<u>(0.2 nm),</u> BUT no information about oxidation state

Combination of LEIS + Chemical Titration:
Provides both composition and oxidation state information of the outer surface atoms

Consequences of Monolayer Sensitivity



LEIS 0.2 nm
depth resolution:
observes

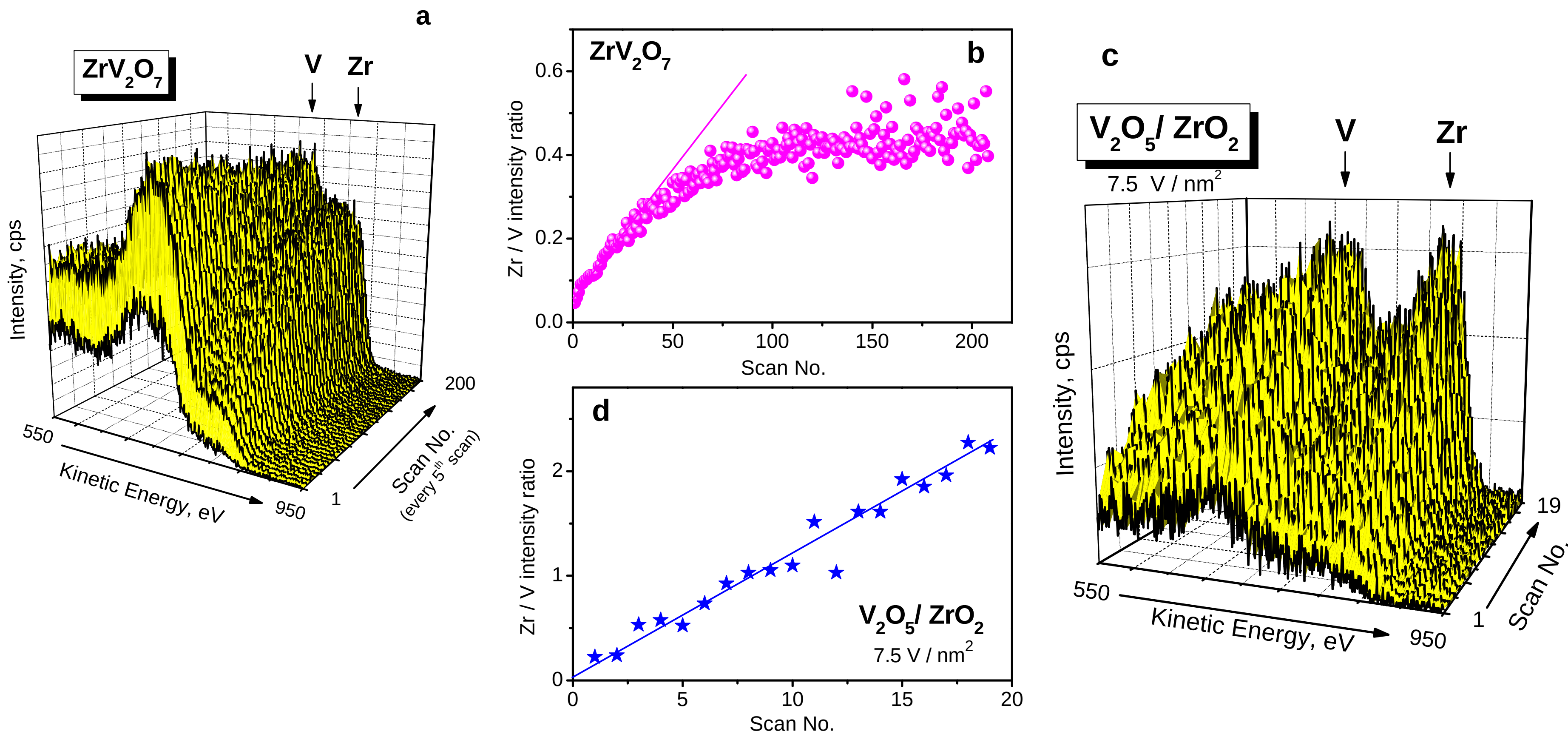
XPS 1-3 nm
depth resolution:
observes

&

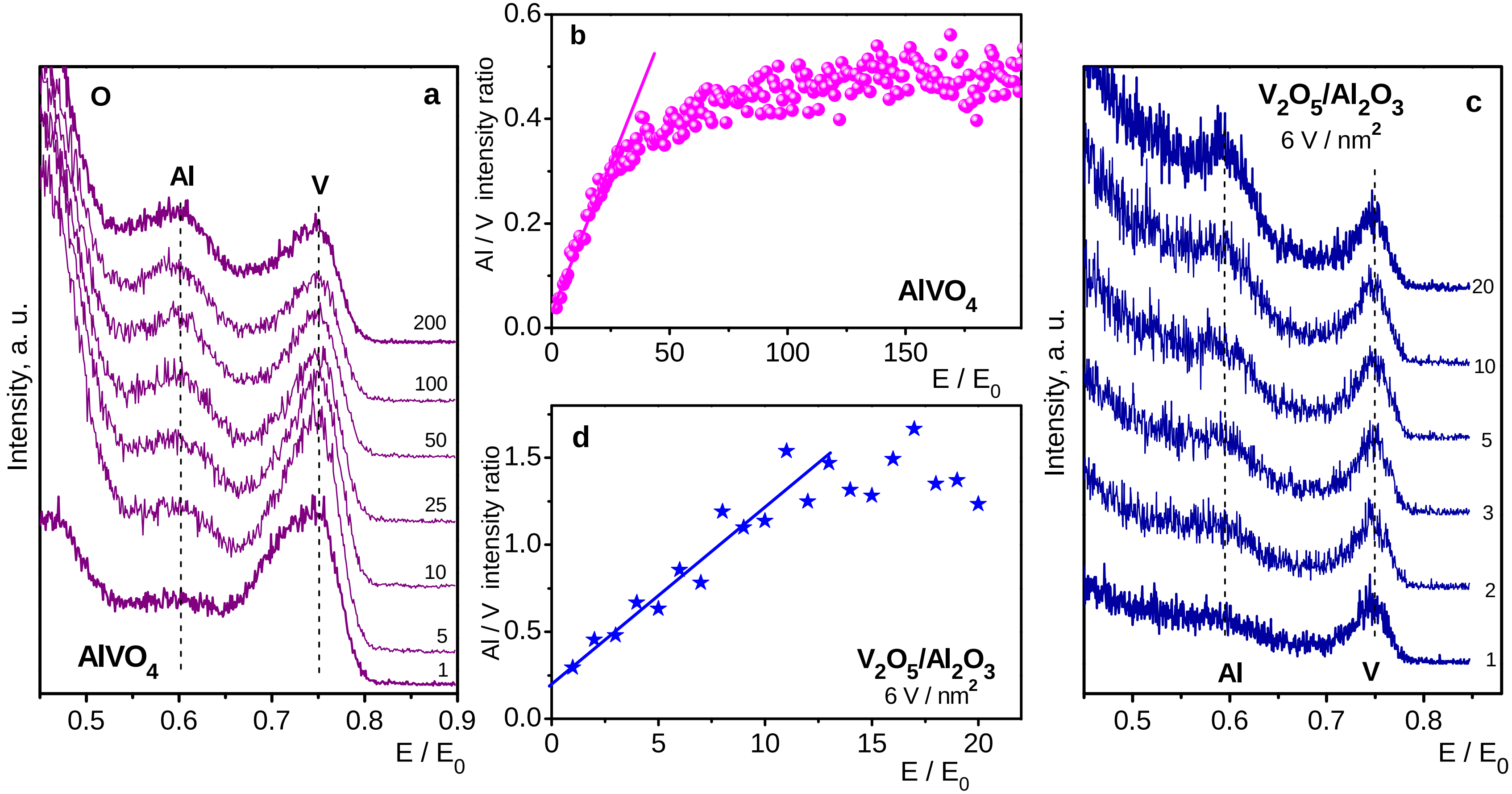
XPS "Surface" Analysis of Stoichiometric Oxides

Oxide (Me = …)	XPS lines used	Stoichiometry Mo/Me (V/Me)	XPS "Surface" Mo/Me (V/Me)[a]
ZrV_2O_7 (Me = Zr)	V $2p_{3/2}$ // Zr 3d	2	2.0
$AlVO_4$ (Me = Al)	V $2p_{3/2}$ // Al 2p	1	0.63
$Ce_8Mo_{12}O_{49}$ (Me = Ce)	Mo 3d // Ce 3d	1.5	2.5
$Fe_2(MoO_4)_3$ (Me = Fe)	Mo 3d // Fe 2p	1.5	1.8
α-$Bi_2Mo_3O_{12}$(K) (Me = Bi)	Mo 3d // Bi 4f	1.5	1.7 (K : Bi = 0.09)
α-$Bi_2Mo_2O_9$(K) (Me = Bi)	Mo 3d // Bi 4f	1	1.4 (K : Bi = 0.10)
γ(H)-Bi_2MoO_6(K) (Me = Bi)	Mo 3d // Bi 4f	0.5	0.33 (K : Bi = 0.10)
$Bi_6Mo_2O_{15}$(K) (Me = Bi)	Mo 3d // Bi 4f	0.33	0.24 (K : Bi = 0.07)
$Bi_{38}Mo_7O_{78}$(K) (Me = Bi)	Mo 3d // Bi 4f	0.18	0.19 (K : Bi = 0.22)
γ(H)-Bi_2MoO_6 (Me = Bi)	Mo 3d // Bi 4f	0.5	0.86
γ(L)-Bi_2MoO_6 (Me = Bi)	Mo 3d // Bi 4f	0.5	0.43
α-$Bi_2Mo_3O_{12}$ (Me = Bi)	Mo 3d // Bi 4f	1.5	1.1

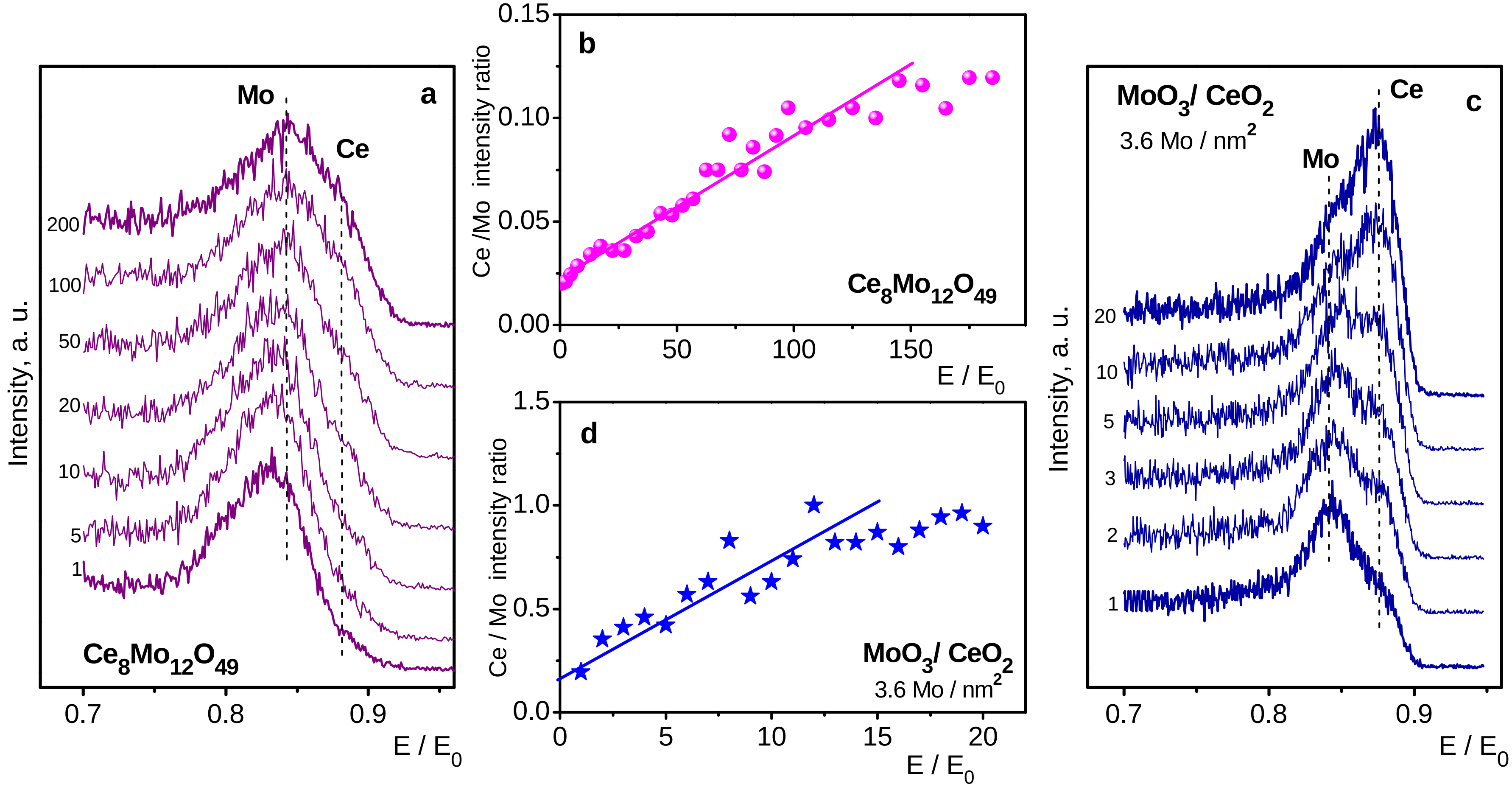
Surface VOx Monolayer Present on ZrV_2O_7!



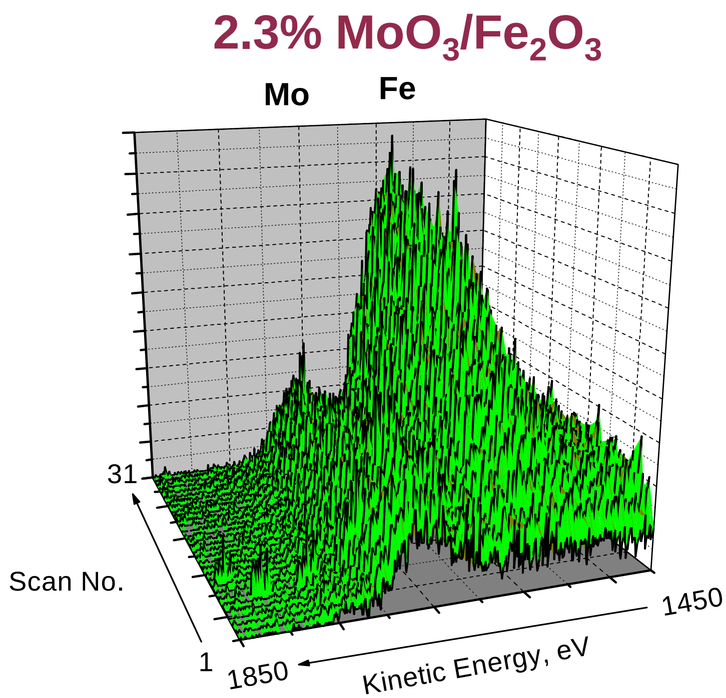
Surface VOx Monolayer Present on $AlVO_4$!

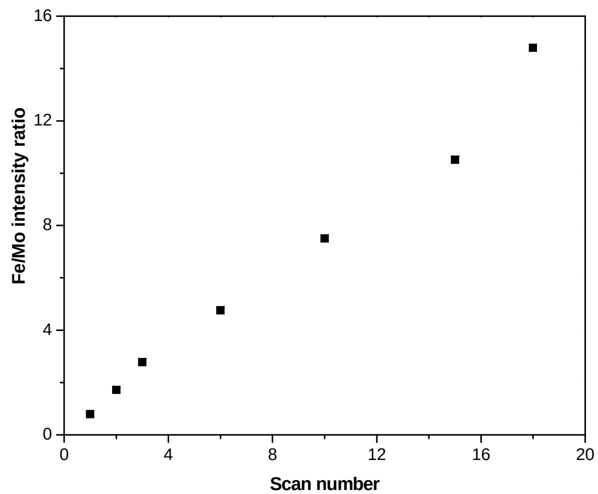


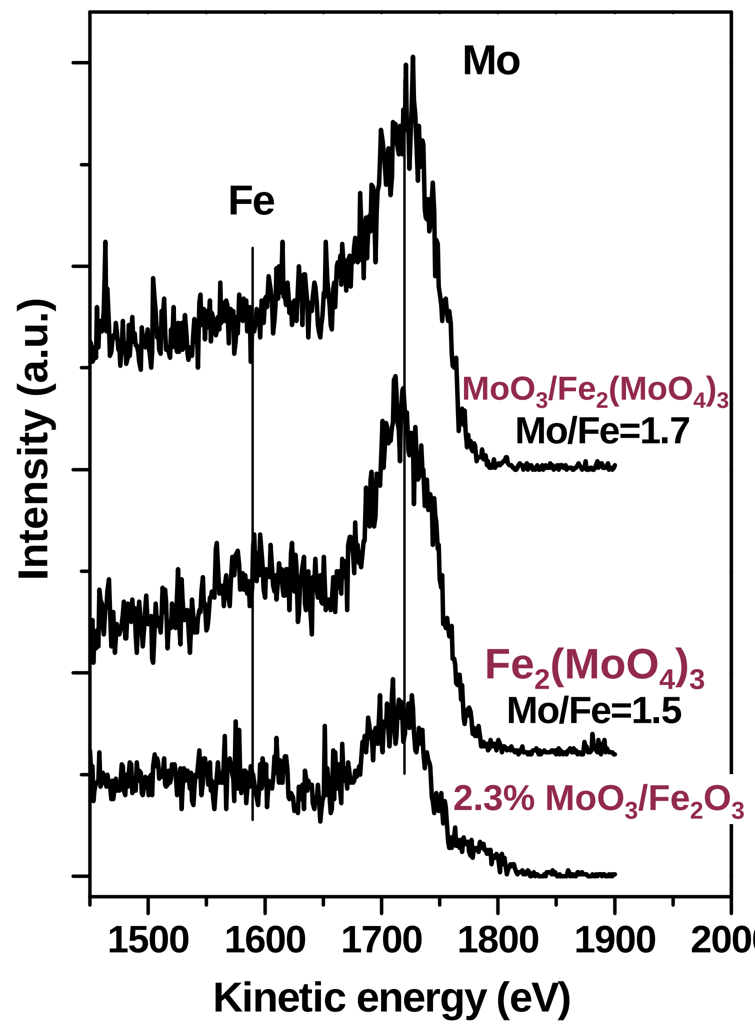
Surface MoOx Monolayer Present on $Ce_8Mo_{12}O_{49}$!



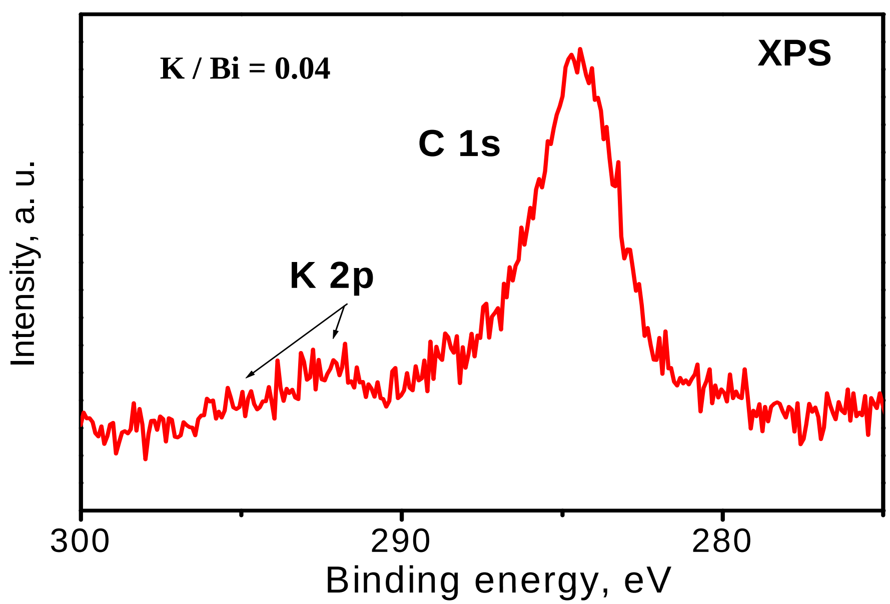
Surface MoOx Monolayer Present on $Fe_2(MoO_4)_3$!

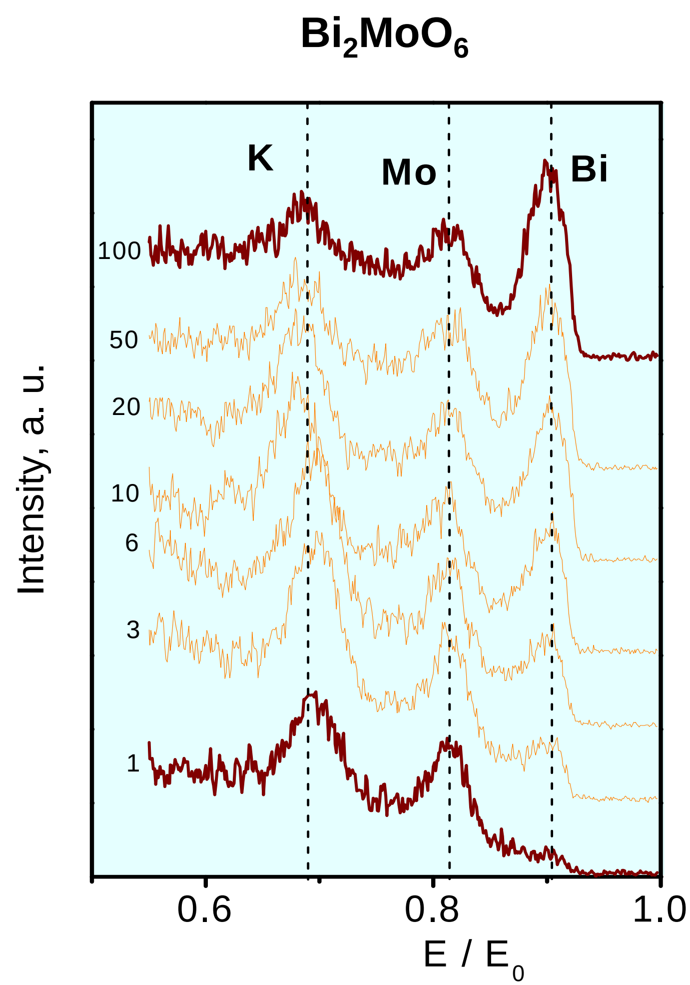






Surface of Bulk Bi-Mo-O Catalyst Does Not Possess Bi and Contaminated with K!





Conclusions

- **Only LEIS provides <u>true surface compositions</u> of stoichiometric oxides**

- **Stoichiometric mixed oxide surfaces enriched in MoOx and VOx due to their low surface energy & surface diffusion (low Tammann Temperatures)**


RETHINK EVERYTHING