F. Garagiola, P.L. Villa, S. Mobilio and G. Vlaic:

Te ENVIRONMENT IN DOPED Fe$_2$ (Mo$_4$)$_3$ BY EXAFS

Estratto da:
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Multicomponent molybdate systems are widely used as catalysts in the oxidation and ammions oxidation of olefins. For this reason a lot of scientific work has been done on such systems. In this chemical composition Te and Bi atoms are generally present, which enhance the activity and selectivity in the catalytic process \cite{1, 2}. Different explanation have been proposed \cite{3-5} in spite of the fact that no direct evidence has been found regarding either the occupied site (substitutional or interstitial) or the oxidation state, or the local environment around the doping atoms.

EXAFS measurement and results are reported on Te L_{III} edge on Te doped Fe_2(MoO_4)_3. Three different compositions have been studied x=0.32, x=0.128 and x=0.256 (x is Te weight in gram per Fe(MoO_4)_3 mole. H_2TeO_6 and TeO_2 in ortorombic and tetragonal phases have been used as model compounds \cite{6}.

Spectra have been recorded on the PULS X-ray beam line in the energy range 4000-4600 eV with a step of 2 eV. Typical Adone current and energy were 50 mA and 1.5 GeV.

Table I reports results obtained by standard data analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>R</th>
<th>Δσ</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2TeO_6</td>
<td>6</td>
<td>1.916</td>
<td>---</td>
<td>----</td>
</tr>
<tr>
<td>Te0.032</td>
<td>8.4</td>
<td>1.93</td>
<td>0.0</td>
<td>-1.4</td>
</tr>
<tr>
<td>Te0.128</td>
<td>8.8</td>
<td>1.93</td>
<td>0.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>Te0.256</td>
<td>8.5</td>
<td>1.93</td>
<td>0.0</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

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Moreover the edge position, which is identical to the $\text{H}_5\text{TeO}_6$ one, clearly shows a $^{+6}$ oxidation state for the Te in the catalysts.

Data of Table I on the Te coordination, exclude the presence of substitutional Te atoms in the matrix since Fe coordination is 6 and Mo coordination is 4. So cavities able to arrange eightfold coordinated Te atoms must be present. Such cavities are not present either in the undoped matrix, nor in the MoO$_3$, generally present as an impurity in all samples.

A possible explanation can be a reorientation of the elementary polyhedra induced by the Te.

References:

(2) P. Forzatti et al., J. Catal. 76, 188 (1982).