The Structure of Rhenium Oxide–Alumina Metathesis Catalysts

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The structure of rhenium(VII) oxide on alumina at loadings of 5 and 17.5% closely resembles that of crystalline rhenium(VII) oxide.

Three models describing the alumina-supported rhenium(VII) oxide structure active in olefin metathesis have been proposed: (i) a surface aluminium mesoperrhenate(VII) structure with surface anion vacancies and F-centres produced by Re^{6+} participation,[1] (ii) a uniform monolayer of Re_2O_7 covering the alumina surface,[2] and (iii) different adsorbed rhenium species

Table 1. Ion fragment intensities relative to ReO_2^-.

Fragment	5% NH_4ReO_4–Al_2O_3	17.5% NH_4ReO_4–Al_2O_3	Re_2O_7	5% Re_2O_7–Al_2O_3	17.5% Re_2O_7–Al_2O_3
ReO^-	0.096	0.04	0.089	0.063	0.07
ReO_2^- [a]	1	1	1	1	1
ReO_3^- [b]	3.48	5.21	17.0	12.3	16.2
ReO_4^- [c]	1.5	2.64	24.5	8.48	9.9
$Re_2O_2^-$			trace		
$Re_2O_3^-$	trace	trace	trace		
$Re_2O_4^-$	0.022	0.020	0.055	0.066	0.021
$Re_2O_5^-$	0.082	0.08	0.23	0.16	0.046
$Re_2O_6^-$	0.036	0.03	0.058	0.03	0.016
$Re_2O_7^-$	0.024	0.02	0.013	trace	trace
$Re_2O_8^-$			0.016		trace
$Re_2O_9^-$			trace	trace	trace
$Re_2O_{10}^-$		0.01	0.016	0.014	0.014
$Re_2O_{11}^-$		trace	trace	trace	trace
$Re_3O_2^-$			trace		
$Re_3O_3^-$				trace	trace
$Re_3O_4^-$			trace	trace	trace
$Re_3O_5^-$		trace	0.011	0.011	trace
$Re_3O_6^-$		trace	0.017	0.014	0.011
$Re_3O_7^-$		0.01	0.046	0.015	0.011
$Re_3O_8^-$		trace	0.016		
$Re_3O_9^-$			0.013		
Re_4O^-			trace		
$Re_4O_2^-$			trace	trace	
$Re_4O_3^-$			trace		

[a] Rel. int. for NH_4ReO_4 = 1. [b] Rel. int. for NH_4ReO_4 = 4.8. [c] Rel. int. for NH_4ReO_4 = 1.06.

depending upon loading, $[ReO_4]^-_{ads}$ up to 13% Re_2O_7, $[Re_2O_7]_{ads}$ greater than 13% Re_2O_7.[3]

We have found that the negative-ion fast-atom bombardment secondary-ion mass-spectra, F.A.B.–S.I.M.S., of supported rhenium species are quantitatively similar to the spectra of the bulk, unsupported compounds. The samples are γ-alumina impregnated with aqueous ammonium rhenate(VII), dried at 110 °C, and subsequently calcined in dry air at 525 °C, producing Re_2O_7. Rhenium loadings are quoted throughout as % wt/wt Re_2O_7.

The intensities of the secondary ion fragments ReO^-, ReO_2^-, ReO_3^-, and ReO_4^-, relative to that of ReO_2^-, Table 1, show quantitative similarities between alumina–NH_4ReO_4 and crystalline NH_4ReO_4 and between alumina–Re_2O_7 and crystalline Re_2O_7. Better correlations are shown for the higher loading samples.

The 5 and 17.5% samples of NH_4ReO_4–alumina also show the presence of significant amounts of Re_2O_7. Exceptionally, the intensity ratios for ReO_4^- and ReO_3^- for supported Re_2O_7 are more similar to that for crystalline NH_4ReO_4 where $ReO_4^- > ReO_3^-$.

Table 2. Intensity ratios for fragments ReO_2 and AlO_2.

	ReO_2^+ : AlO^+		ReO_2^- : AlO^-	
	^{185}Re	^{187}Re	^{185}Re	^{187}Re
5% NH_4ReO_4–Al_2O_3	0.055	0.0043	0.023	0.041
17.5% NH_4ReO_4–Al_2O_3	0.0123	0.0191	0.152	0.248
5% Re_2O_7–Al_2O_3	0.0116	0.0092	0.106	0.152
17.5% Re_2O_7–Al_2O_3	0.0081	0.0110	0.096	0.149

The lattice of discrete ReO_4^- tetrahedra would not produce significant secondary clusters containing more than one rhenium atom. In contrast the molecular chain structure of Re_2O_7 should and does produce characteristic $Re_xO_y^-$ fragments with $Re_2O_5^-$ and $Re_3O_7^-$ predominating in intensity.

We conclude that decomposition of NH_4ReO_4 on alumina produces aggregates of Re_2O_7 lying on ReO_4^- clusters which are in intimate contact with the alumina. While this is at variance with previously proposed models, it is confirmed by similar studies of chromium oxide catalysts.[4]

Secondary cluster ions containing both Re and Al atoms were not observed although cluster ions from the support alone were common. There is therefore no evidence for aluminium mesoperrhenate structures or for Re_2O_7 monolayer formation.

The intensity ratios ReO_2 : AlO for both positive and negative ions show, Table 2, that for alumina–NH_4ReO_4 samples a marked increase occurs from 5 to 17.5% Re_2O_7 while for alumina–Re_2O_7 the ratio is independent of loading. During impregnation the surface coverage of adsorbed NH_4ReO_4 increases with loading but during calcination production of Re_2O_7 proceeds, increasing the depth of aggregation so that the exposed surfaces of rhenium and aluminium oxides are the same at both loadings.

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