Electron Spin Resonance Spectra of Molybdenum in Zeolite Y

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Summary E.s.r. spectra of $Mo(CO)_6$ adsorbed in zeolite Y show formation of molybdenum(I) and molybdenum(V) on heating *in vacuo* or on exposure to O_2.

Transition metal exchanged zeolites have been extensively used as heterogeneous catalysts.[1] Zeolites also provide a convenient framework in which to study the co-ordination chemistry of transition metal ions in well defined surface environments.[2] A catalytically important transition metal which has not been examined in zeolites is molybdenum, since the absence of any stable low oxidation state ions has prevented conventional solution ion-exchange methods from being used to prepare molybdenum zeolites. Gallezot *et al.*[3] recently described the preparation of a molybdenum loaded zeolite Y from adsorbed $Mo(CO)_6$, in an interesting development of the earlier reported procedure[4] for preparing silica or alumina supported molybdenum catalysts from $Mo(CO)_6$. We now report some preliminary results of an e.s.r. spectroscopic study of molybdenum loaded zeolite Y undertaken with the intention of identifying the intrazeolitic molybdenum species produced by this method.

Molybdenum Y zeolite was prepared following the method of Gallezot *et al.*[3] by adsorbing $Mo(CO)_6$ vapour at room temperature into an HY zeolite to give a loading of 8 $Mo(CO)_6$ molecules per unit cell. E.s.r. spectra were then recorded as a function of subsequent *in situ* treatment.

Representative Q-band spectra are shown in the Figure (recorded at 300 K). Initial adsorption of $Mo(CO)_6$ into the zeolite did not give any paramagnetic species. On subsequent heating *in vacuo*, however, a number of different e.s.r. signals appeared. Comparison of Q and X-band spectra indicates that all the features shown in the Figure are the result of a g-tensor anisotropy, not molybdenum hyperfine splitting. After treatment at temperatures below 500 K, 2 signals with $g_\perp$ values > 2 appeared (Figure, A). At higher temperatures these signals were progressively removed and signals appeared at higher field with $g_\perp < 2$ (Figure, B and C). The same effect could be achieved by exposing low temperature treated samples to oxygen at room temperature *i.e.* the disappearance of the $g_\perp > 2$ signals is an oxidative process. Once removed by high temperature vacuum treatment or by room tempera-

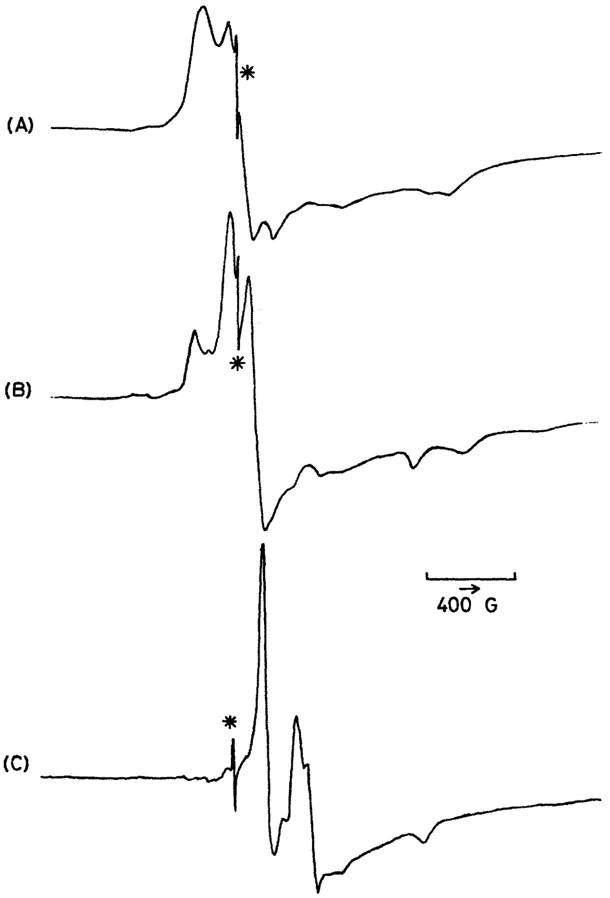

FIGURE. 35 GHz E.s.r. spectra of $Mo(CO)_6$ in HY after heating *in vacuo* at (A), 473 K, 1 h; (B), 573 K, 1 h; (C), 673 K, 1 h (all spectra recorded with the same spectrometer gain). * Denotes diphenylpicrylhydrazyl reference (g = 2·0036).

ture oxidation, the initially formed signals could not be restored by reduction in hydrogen at 750 K. Heating in oxygen at 750 K removed all e.s.r. signals, and subsequent reduction restored only the signals with $g_\perp < 2$.

TABLE. E.s.r. parameters of observed signals

Signal	$g_\perp$	$g_\parallel$	Assignment
I	2·041	Not resolved	Mo^I
II	2·009	1·859	
III	1·99	1·802	Mo^V
IV	1·966	1·926	
V	1·958	1·873	
	1·951		

The e.s.r. parameters of the observed signals are summarized in the Table, together with our proposed assignments. Signals I—V represent pairs of $g_\perp$ and $g_\parallel$ values which appeared to grow and decay together, although these assignments do not account for all the observed features in the *Q*-band spectra. The signals appearing after high temperature treatment are readily assigned to Mo^V species, from their similarity to signals obtained from reduced silica or alumina supported MoO_3 catalysts.[5] At least 3 different Mo^V species are present in the zeolite, presumably occupying different cation sites. These sites are not located on the exterior surface, since the Mo^V signals were not broadened by exposure to a high pressure of oxygen at room temperature. The low field signals appearing after low temperature treatment are tentatively assigned to Mo^I species. The appearance of these signals upon mild heat treatment of Mo^0 and their irreversible removal on further heating or exposure to oxygen suggest they are due to oxidation states lower than V, and the g-tensor values ($g_\perp > 2$, $g_\parallel < 2$) are consistent with a low spin d^5 configuration.[6]

The detailed chemistry of molybdenum in zeolite Y has still to be worked out. The e.s.r. data presented here do, however, confirm the suggestion of Gallezot *et al.* that $Mo(CO)_6$ in HY is oxidized on heating *in vacuo*. The oxidized MoY allows the possibility of studying the co-ordination chemistry of Mo^V in a well defined surface environment. We may expect, for example, to model the active sites on a conventional molybdena–alumina catalyst with intrazeolitic Mo^V complexes. The zeolite is also able to stabilize low oxidation state molybdenum ions such as Mo^I to an appreciable extent.

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