Silica-supported tantalum clusters: catalyst for alkane conversion†

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Silica-supported tantalum clusters (on average, approximately tritantalum) were formed by the treatment, in either H_2 or ethane, of adsorbed $Ta(CH_2Ph)_5$; the supported catalyst is active for ethane conversion to methane and propane at 523 K, with the used catalyst containing clusters of the same average nuclearity as the precursor.

Metal clusters on supports are widely used as catalysts, but these have been restricted almost entirely to group-8 metals and do not include early transition metals. We now report the first supported early transition metal clusters, tantalum on SiO_2, formed under conditions similar to those reported for the synthesis of tantalum clusters in solution; the supported catalyst is active for alkane conversion.

The catalysts were synthesized by adsorbing $Ta(CH_2Ph)_5$ from a solution of mixed hexanes onto the surface of SiO_2 (Degussa Aerosil 200, partially dehydroxylated at 773 K, BET surface area approximately 200 m^2 g^{-1}), giving a pale yellow powder containing 1.2 wt% Ta. This sample was treated in flowing H_2 at 523 K and 1 bar to yield a brown powder. The maxima in the UV-vis spectrum of this sample is in the 300–400 nm range, confirming the presence of Ta–Ta bonds, as in $[(Me_6C_6)_3Ta_3Cl_6]^+$ (λ_{max} = 364, 288 nm),[1] $[(Me_6C_6)_3Ta_6Cl_{12}]^{4+}$ (λ_{max} = 354 nm)[1] and $[Ta_6Cl_{12}]^{n+}$ (for n = 2, 3 or 4; λ_{max} = 334, 344 or 369 nm, respectively),[2] for example. A band in the far-IR spectrum at 148 cm^{-1} confirms the presence of Ta–Ta bonds and hence clusters, with the frequency nearly matching that of $[Ta_6Cl_{12}]^{n+}$ (n = 2, 3 or 4; 140 cm^{-1}), for example.[3] These UV-vis and IR features were absent from the spectrum of SiO_2 alone, and from that of the SiO_2-supported mononuclear tantalum complex formed initially from $Ta(CH_2Ph)_5$.

A quantitative structural characterisation of the supported clusters was carried out by extended X-ray absorption fine structure (EXAFS) spectroscopy (Fig. 1, Fig. 2 and Table 1). The data confirm the presence of Ta–Ta bonds and determine a Ta–Ta coordination number of approximately 2, consistent with supported clusters of approximately 3 Ta atoms each, on average, with a Ta–Ta distance of 2.92 Å, indicated by the corresponding peak in the phase- and amplitude-corrected Fourier transform of the difference spectrum (Fig. 1A). This distance is comparable with Ta–Ta distances in tritantalum clusters synthesized in solution, such as $Ta_3Cl_{10}(PEt_3)_3(HPEt_3)$ (2.932 Å),[4] $Ta_3Cl_9(THF)_4 \cdot C_6H_6 \cdot$ THF (2.868 and 2.850 Å; THF is tetrahydrofuran)[5] and $Na[Ta_3Cl_{10}(THF)_3]$ (2.875 Å).[5]

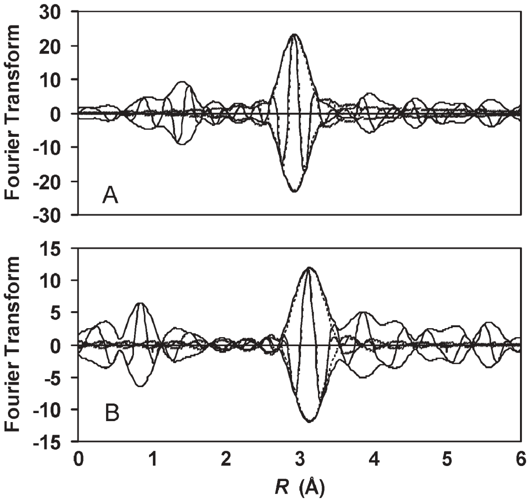

Fig. 1 Phase- and amplitude-corrected Fourier transforms of the Ta–Ta contribution to the EXAFS spectra characterising the samples treated in H_2 (A, solid line) and ethane (B, solid line). Dotted lines represent the Ta–Ta fits; all contributions, except the Ta–Ta contribution, were subtracted from the experimental spectra prior to Fourier transformation.

The EXAFS Ta–Ta contribution was attenuated as a consequence of the presence of phase cancellation caused by the Ta–Si contribution. The phase cancellation was dominant up to values of the wave vector $k \approx 9.5$ $Å^{-1}$; at values greater than this, the effect of phase cancellation became negligible. Thus,

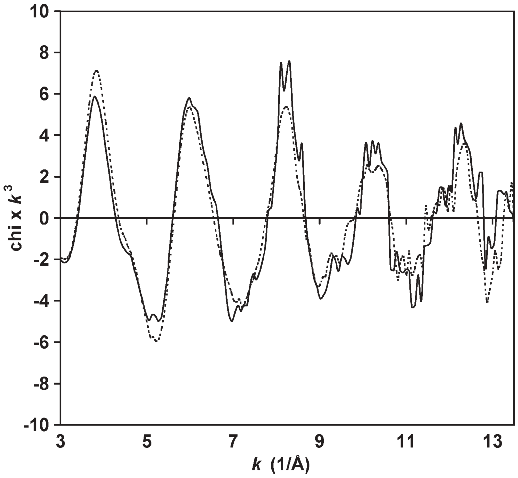

Fig. 2 Experimental k^3-weighted EXAFS spectra of the sample treated in ethane (dotted line) and the used catalyst (solid line). Each spectrum is the average of four scans.

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Table 1 EXAFS parameters characterising the SiO_2-supported samples prepared by adsorption of $Ta(CH_2Ph)_5$, followed by various treatments and their use as catalysts for ethane disproportionation[a]

Sample	Absorber–back-scatterer pair	N	R/Å	$10^3 \times \Delta\sigma^2$/Å^2	ΔE_0/eV
After treatment in H_2 at 523 K	Ta–Ta	2.3 (0.1)	2.92 (0.01)	3.3 (0.6)	−1.7 (1.0)
	Ta–O	3.2 (0.1)	1.91 (0.00)	2.3 (1.9)	−9.2 (0.3)
	Ta–Si	3.4 (0.0)	3.19 (0.01)	1.0 (0.6)	7.4 (0.6)
	Ta–O_{long}	0.9 (0.2)	2.52 (0.01)	0.9 (1)	8.4 (4)
After treatment in ethane at 523 K	Ta–Ta	2.6 (0.1)	3.11 (0.01)	5.5 (0.6)	−2.0 (1)
	Ta–O	4.4 (0.1)	1.90 (0.00)	4.7 (0.3)	−4.2 (0.3)
	Ta–Si	3.5 (0.1)	3.56 (0.01)	7.8 (0.6)	−4.4 (0.6)
	Ta–O_{long}	0.9 (0.2)	2.66 (0.01)	0.8 (1)	5.5 (4)
After treatment in H_2 at 523 K followed by the catalysis of ethane disproportionation at 523 K	Ta–Ta	2.5 (0.1)	3.10 (0.01)	6.7 (0.2)	−3.1 (1.1)
	Ta–O	4.2 (0.1)	1.89 (0.00)	2.8 (0.1)	−2.3 (0.3)
	Ta–Si	3.2 (0.1)	3.52 (0.01)	7.8 (0.2)	−1.6 (0.4)
	Ta–O_{long}	1.0 (0.3)	2.61 (0.01)	4.5 (0.4)	7.1 (2)

[a] Notation: N = coordination number, R = distance between absorber and back-scatterer atoms, $\Delta\sigma^2$ = Debye–Waller factor and ΔE_0 = inner potential correction. Numbers in parentheses are the errors determined from repeat scans and represent precisions, not accuracies. Estimated accuracies are as follows: Ta–Ta: $N \pm 20\%$, $R \pm 0.02$ Å, $\Delta\sigma^2 \pm 20\%$, $\Delta E_0 \pm 20\%$; Ta–O: $N \pm 30\%$, $R \pm 0.02$ Å, $\Delta\sigma^2 \pm 25\%$, $\Delta E_0 \pm 20\%$; Ta–Si: $N \pm 50\%$, $R \pm 0.03$ Å, $\Delta\sigma^2 \pm 30\%$, $\Delta E_0 \pm 20\%$. The subscript "long" represents the longer of the two Ta–O contributions.

acquisition of data at values of k exceeding approximately 10 Å^{-1} was critical in resolving the EXAFS Ta–Ta contribution.

The synthesis of SiO_2-supported clusters was also carried out by using ethane in the treatment instead of H_2. When the sample formed initially from $Ta(CH_2Ph)_5$ was treated in flowing ethane at 523 K and 1 bar, again it turned brown, and EXAFS spectroscopy indicated a Ta–Ta contribution at 3.11 Å (Fig. 1B) with a coordination number of about 2, again indicating the presence of approximately trinuclear clusters. The Ta–Ta distance in the sample treated in H_2 is less than that of the sample treated in ethane (Table 1). As diminution of metal–metal bond lengths results from the reduction of group-5 metal clusters,[4] we suggest that the shorter Ta–Ta bond length in the H_2-treated clusters corresponds to their greater degree of reduction in H_2 than in ethane.

Taken together, these results demonstrate the formation of tantalum clusters on SiO_2 and that the conditions of the synthesis on this support approximately match those of syntheses of comparable clusters in solution,[5] indicating that the solution and surface chemistries are analogous.

The supported samples were tested as catalysts of ethane conversion. Particles of the H_2-treated sample (0.5 g) were loaded into a once-through plug-flow reactor, connected to an online GC equipped with a gas sampling valve for product analysis. When ethane at a partial pressure of 36 mbar in He (total pressure = 1 bar) flowed through the bed of powder at 523 K at a rate of 8 mL (NTP) min^{-1}, the catalytic formation of methane and propane was observed. The initial conversion of ethane was 24%. The molar ratio of methane to propane exceeded 1, and small quantities of butanes were also observed. Specifically, for example, after 22 h time on-stream (TOS), the selectivity to methane was 56% (molar), with the remainder being predominantly propane (approximately 42%), along with butanes, but no detectable higher alkanes. After this TOS, the number of ethane molecules converted per Ta atom was 21. Similarly, in separate experiments, propane fed to the reactor was converted into butanes and ethane, as well as small amounts of methane (with a higher selectivity at lower TOS values than at higher TOS values) and pentanes.

The product distributions indicate alkane disproportionation, both of the feed alkane and in secondary reactions of the higher alkane products. The catalyst underwent deactivation with TOS, and most of its activity had been lost after 20 h. When the feed was ethane, the total number of ethane molecules converted per Ta atom was 21. The used catalyst was brown, matching the colour of the sample introduced into the reactor.

EXAFS analysis of the used ethane conversion catalyst, treated as air-sensitive (as were all the samples), still indicated the presence of tantalum clusters with an average nuclearity of approximately 3; the Ta–Ta distance was 3.10 Å (Table 1), nearly matching the Ta–Ta distance in the clusters synthesized directly from ethane. Moreover, the full EXAFS spectra of the used catalyst and that of the sample treated in ethane are nearly the same, as are the EXAFS fit parameters (Fig. 2 and Table 1), indicating that nearly the same supported species were present in each.

We tentatively associate the loss of catalytic activity with the increase in the Ta–Ta bond length, which is indicative of an increase in the cluster oxidation state.[6] Maintaining the clusters in a reduced state may minimise losses in catalytic activity. Moreover, changes in the oxidation state of tantalum in clusters is reversible,[7] and this redox chemistry opens up the possibility of regenerating oxidized clusters, for example, by using H_2 as a reductant.

The disproportionation of alkanes is a reaction known to be catalysed by strong solid acids (such as aluminium chloride supported on a sulfonic acid resin[8]) and by classic bifunctional (tandem) catalysts consisting of platinum supported on alumina (which catalyses dehydrogenation of the alkane) mixed with tungsten oxide on alumina (which catalyses metathesis of the resultant alkene); rehydrogenation occurs on the platinum.[9] A related soluble catalytic system, consisting of a platinum complex for dehydrogenation/hydrogenation and a Schrock-type alkene metathesis catalyst, gives higher- and lower-molecular weight alkanes from *n*-hexane.[10] Such a reaction has also been observed to occur at 423 K by a similar route (with alkenes and H_2 as the primary products) catalysed by a SiO_2-supported sample, reported on the basis of EXAFS analysis to consist of mononuclear tantalum complexes.[11]

In summary, the data reported here demonstrate the formation of approximately trinuclear tantalum clusters on SiO_2; the material catalyses alkane disproportionation. This is the first report of supported clusters of an early transition metal and their catalytic properties.

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