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Silica-supported tantalum clusters: catalysts for conversion of methane with *n*-butane to give ethane, propane, and pentanes

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$Si0_2$-supported tantalum clusters were prepared by adsorption of the precursor $Ta(CH_2Ph)_5$ (Ph is phenyl) on the support followed by treatments in H_2 at 523, 623, and 723 K. The resultant clusters, had approximate average diameters of 0.3, 0.8, and 2 nm, as determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. The samples were tested as catalysts for conversion of methane with *n*-butane in a once-through flow reactor operated at atmospheric pressure and 523 K, and EXAFS spectroscopy was used to characterize the used catalysts. The results show that (a) the catalysts are active for the conversion of methane with *n*-butane to give ethane, propane, and pentanes; (b) catalytic activity decreased to nearly zero over a time on stream of 22 h; (c) the catalyst incorporating the smallest clusters exhibited the highest initial activity and that incorporating the largest clusters exhibited the lowest activity; (d) each used catalyst contained clusters of approximately the same nuclearity as the respective fresh catalyst, but with Ta–Ta bond lengths approximately 0.17 Å longer than those found in the fresh catalysts. The data are consistent with catalysis by the supported clusters, and the product distributions are consistent with disproportionation of *n*-butane accompanied by the reaction of methane with propane to give other alkanes.

KEY WORDS: conversion of methane + *n*-butane; supported tantalum clusters.

1. Introduction

Methane from natural gas is a plentiful hydrocarbon resource, used on an enormous scale in steam reforming and autothertnal reforming processes to make synthesis gas for the production of chemicals and, increasingly, fuels. With the forthcoming application of large-scale gas-to-liquids processes for conversion of natural gas via synthesis gas, followed by Fischer-Tropsch synthesis and hydrocracking of the resultant hydrocarbons, there is expected to be a large increase in the availability of light alkalies. Extensive research has been carried out with the goal of discovering new routes for the conversion of light alkanes, such as by partial oxidation, although with limited success. We now report a new catalyst, SiO_2-supported tantalum clusters, for the conversion of methane with light alkalies (illustrated by *n*-butane) into alkalies of intermediate and higher molecular weights.

2. Experimental methods

2.1. Catalyst synthesis

SiO_2-supported tantalum clusters of various sizes were formed by adsorbing $Ta(CH_2Ph)_5$ (Ph is phenyl) on the surface of SiO_2 (Degussa Aerosil 200, partially dehydroxylated at 773 K, BET surface area approximately 200 $m^2\ g^{-1}$) from a solution of mixed hexanes, giving a pale yellow powder containing 1.2 wt% Ta. This sample was treated in flowing H_2 at various temperatures (523, 623, or 723 K) and 1 bar to yield brown powders containing tantalum clusters. Details of the synthesis are described elsewhere [1].

2.2. Methane conversion with n-butane in a flow reactor

Catalytic reaction experiments were carried out with a once-through flow reactor system equipped with mass flow controllers, an online gas chromatograph, and freshly regenerated traps for the removal of traces of oxygen and moisture. Methane (Puritan; 5% balance argon) and *n*-butane(Airgas, 99.9%) or H_2 (Airgas, 99.999%) were used as feeds. Each catalyst sample (500 mg) was loaded into the reactor in an argon-filled glovebox and transferred under argon to the flow system, which had previously been purged with He. The catalyst was subsequently treated at 523, 623, or 723 K in flowing H_2 at 1 bar. After treatment for 20 h, the reactor was purged with He, and the temperature was adjusted, if necessary, to 523 K prior to the beginning of reactant flow (6.4 mL/min total flow at NPT; 4.9 mol% methane and 2.2 mol% *n*-butane).

The reactor effluent was analyzed by gas chromatography (HP 5890; 50 m × 0.53 mm × 15μm HP PLOT $A1_20_3$ column) equipped with an automated online gas-sampling valve. Prior to the start of a

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catalytic reaction experiment (and immediately after each such experiment), the reactant concentrations were determined by analysis of the feed gas. Conversions of methane and conversions to ethane, propane, and pentanes were determined quantitatively; conversions of butanes are not reported quantitatively, because they were small and characterized by relatively large errors.

Upon termination of a catalytic reaction experiment, the reactor was cooled to ambient temperature while being purged with He, and then it was transferred to the glovebox, where the used catalyst was stored.

2.3. Catalyst characterization by extended X-ray absorption fine structure (EXAFS) spectroscopy

Fresh and used catalysts were characterized by EXAFS spectroscopy. The measurements were made at beamline 2–3 of the Stanford Synchrotron Radiation Laboratory (SSRL) of the Stanford Linear Acclerator Center, Stanford, CA, and at beamline X-18B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, NY. The storage ring electron energy was 3 GeV at SSRL and 2.6 GeV at NSLS; the ring current varied within the range of 50–100 mA at SSRL and 140–240 mA at NSLS. EXAFS data were recorded at the Ta L_{III} edge with samples (pressed selfsupporting wafers, 120 mg each), which were stored in a nitrogen-filled glovebox at each synchrotron, in which they were loaded into a transmission cell equipped with beryllium windows. The cell [2] was mounted in the beam (as contact of the sample with air was prevented) and evacuated to a pressure of approximately 1.3×10^{-6} mbar and cooled to liquid-nitrogen temperature prior to data collection. Higher harmonics in the X-ray beam were minimized by detuning of the monochromator by 20–25% at the Ta L_{III} edge. The resolution of the monochromator was 0.5 eV. Four scans were recorded for each sample, simultaneously with spectra of tantalum foil for calibration of the energy at the Ta_{III} edge.

3. Analysis of EXAFS data

The software XDAP [3] was used to deglitch the data, subtract the background, and normalize the data to give the experimental EXAFS (chi) function. The normalized EXAFS function characterizing each sample is the average of four scans. XDAP was used to analyze the EXAFS data with a difference file technique. The functional that was minimized and the function used to model the data are given elsewhere [4]. The postulated structural models used in the data fitting included Ta–Ta, Ta–O, and Ta–Si contributions. Reference backscattering amplitudes and phase shifts characterizing these contributions were calculated with the software FEFF7 [5] from crystallographic coordinates of the unit cells of the following known reference compounds: Ta [6], Ta_2Si [7], and Ta_20_5 [8]. The amplitude reduction factor was determined to be 0.95 by fitting the spectrum of tantalum foil by using the FEFF-generated reference for tantalum metal; this value was used in the analyses of the spectra of the supported samples.

Analysis was carried out with the unfiltered EXAFS data. The maximum statistically justified number of free parameters in the analysis was estimated on the basis of the Nyquist theorem; this number of parameters was always greater than the 16 used in the fit of the data for each sample. Iterative fitting was done both in k-space and in r-space by using k^1- and k^3-weightings until optimum agreement was obtained between the data and the fits, with both k^1- and k^3-weightings considered (k is the wavevector and r is the absorber-backscatterer distance).

4. Results

4.1. Catalytic reaction of methane with n-butane

Each of the catalyst samples (treated at 523, 623, or 723 K) was active for conversion of methane + n-butane. Conversion of methane as a function of time-on-stream (TOS) in the flow reactor is shown in figure 1 for the sample treated at 523 K. Methane conversion decreased with TOS; the initial conversion, determined by an extrapolation to TOS = 0, was 7.7%. The decrease in conversion was roughly exponential after 4 h; after 12 h, the conversion had decreased to 1%. Experiments were stopped when methane conversion was no longer detectable within the scatter of the data.

The conversions are inferred to have been catalytic on the basis of the number of methane molecules converted per Ta atom over the course of each experiment; for example, the total number of methane molecules converted per Ta atom (defined as the number of turnovers, NOT) representing the sample treated at 523 K was 15 (table 1). The NOT, as well as the initial rate of methane conversion, decreased with increasing temperature of catalyst pretreatment in H_2 (figure 2, table 2). We

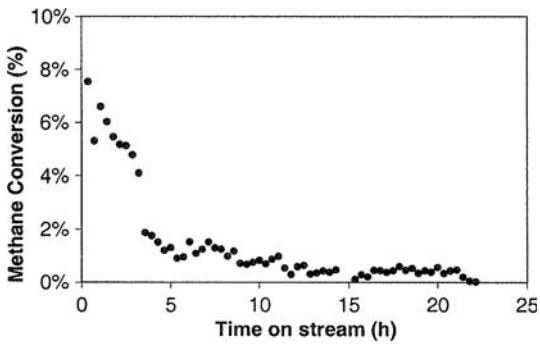

Figure 1. Conversion of methane as a function of time on stream (TOS) representing the sample treated at 523 K.

Table 1
Activities of supported tantalum cluster catalysts for the conversion of methane with *n*-butane.[a]

Tempeature of sample pretreatment in H_2(K)	Intial conversion of methane (%)	$10^4 \times$ initial rate of methane conversion[b] (mol of methane converted/ (mol of Ta × s)	NOT[c]
523	7.7	7.6 ± 11.0	15 ± 2.2
623	3.5	2.1 ± 0.9	5.2 ± 2.1
723	2.5	1.8 ± 1.2	3.4 ± 2.5

[a] Errors represent the scatter In the data in individual experiments.
[b] Initial rate of catalytic reaction and initial conversion determined by extrapolation to zero time on stream. The 500-mg catalyst samples were pretreated at 523, 623, or 723 K, each for 20 h; reaction conditions: 6.4 mL/min total flow rate of reactants (4.9 mol% methane and 2.2 mol% *n*-butane in helium) at 523 K and 1 atm.
[c] Number of turnovers (NOT) repported as moles of reactant conaumed per mol of Ta during time on stream.

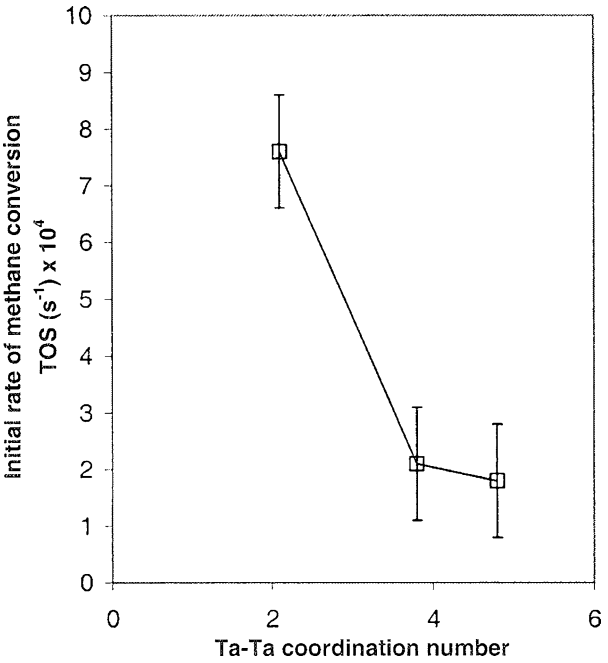

Figure 2. Initial rate of methane conversion as a function of Ta–Ta coordination number as determined by EXAFS spectroscopy. The 500-mg catalyst samples were pretreated at 523, 623, or 723 K, each for 20 h; reaction conditions: 6.4 mL/min total flow rate of reactants (4.9 mol% methane and 2.2 mol% *n*- butane in helium) at 523 K and 1 atm.

estimate the initial ratio of conversion of methane to conversion of butane (determined from the initial amounts of pentane and propane produced) to be approximately 60.

The products of the catalytic reaction were ethane, propane, and pentanes, and the selectivity changed with time on stream (figure 3). Specifically, for example, when the catalyst had been treated in H_2 at 523 K, propane and pentanes were the predominant products at TOS < 4 h. The selectivity for propane formation decreased until it became indistinguishable from zero after 4 h TOS; the selectivity for formation of pentanes initially increased, then began to decrease after 4 h TOS, when the methane conversion had decreased from 8–4%. After 4 h TOS, the selectivity for ethane began to increase, reaching nearly 100% after 12 h; methane conversion was then 1%. After 12 h, the selectivity for ethane formation decreased, becoming indistinguishable from zero after about 19 h. Selectivity to propane (which had been indistinguishable from zero at values of TOS between 4 and 11.5 h) began to increase, until it was the only observable product after 19 h. The selectivity to pentane remained indistinguishable from zero when TOS was >13 h. Methane. conversion after 19 h was 0.4% [9].

The qualitative trends in product selectivity did not vary with the pretreatment temperature of the catalyst.

4.2. *EXAFS characterization of supported tantalum catalysts*

Analysis of the EXAFS spectra characterizing the unused catalysts treated in H_2 at various temperatures (523, 623, and 723 K) indicated the presence a Ta–Ta shell in the spectrum of each sample, as evidenced by the position of the peak at 2.93 Å in the symmetric Ta–Ta phase- and amplitude-corrected Fourier transform of the experimental spectra (figure 4; the best-fit Ta–O, Ta–Si, and Ta–O_{long} contributions were subtracted from these spectra) [1]. The EXAFS data also indicate a Ta–O contribution with a coordination number of approximately 3, at a distance of 1.91 Å; this is a bonding distance [1]. Details of the EXAFS results characterizing the samples treated in H_2 at 523, 623, and 723 K are given elsewhere [1, 10].

The magnitude of the Fourier transform (figure 4) characterizing the Ta–Ta contribution increased with increasing treatment temperature, indicating that the Ta–Ta coordination number increased with increasing temperature of treatment in H_2 [1]. The corresponding Ta–Ta first-shell coordination numbers were found to be 2.1, 3.8, and 4.8 for the samples treated at 523, 623, and 723 K, respectively, corresponding roughly to average cluster diameters of 0.3, 0.8, and 2 nm, respectively, assuming a raft like geometry of the clusters—we infer the presence of raft-like structures because the Ta–O coordination number remained nearly unchanged as the

Table 2
EXAFS parameters characterizing the samples after use as methane conversion eatalysts.[a]

Temperature of sample pretrtreatment in H_2, K	Absorber backscatterer pair	N	$R(')$	$10^3 \times \triangle\sigma^2(^2)$	$\triangle E_0$ (eV)
523	Ta–Ta	2.4 ± 0.3	3.08 ± 0.01	5.8 ± 0.4	−4.4 ± 1
	Ta–O	4.2 ± 0.1	1.90 ± 0.00	5.5 ± 0.1	−9.4 ± 0.2
	Ta–Si	2.1 ± 0.2	3.38 ± 0.01	7.7 ± 0.7	−9.8 ± 0.3
	Ta–O_{long}	0.5 ± 0.2	2.66 ± 0.03	8.3 ± 0.6	−7.9 ± 2.8
623	Ta–Ta	3.8 ± 0.2	3.10 ± 0.01	8.5 ± 0.6	−2.4 ± 1.2
	Ta–O	4.1 ± 0.0	1.89 ± 0.00	3.9 ± 0.1	−4.3 ± 0.4
	Ta–Si	2.7 ± 0.1	3.53 ± 0.01	7.5 ± 0.6	−2.6 ± 0.6
	Ta–O_{long}	1.2 ± 0.1	2.67 ± 0.03	7.9 ± 0.1	−0.9 ± 2.6

[a] Notation: N = coordination number; R = distance between absorber and backscatterer atoms; $\triangle\sigma^2$ = Debye Waller factor; $\triangle E_o$ = inner potential correction. Numbers in parentheses are the calculated errors and represent precisions, not accuracies. Estimated accuracies are as follows: Ta–Ta: N ± 20%, R ± 0.02 Å, $\triangle\sigma^2$ ± 20%, $\triangle E_0$ ± 20%; Ta–O: N ± 30%, R ± 0.02 Å, $\triangle\sigma^2$ ± 25%, $\triangle E_o$ ± 20%; Ta–Si: N ± 50%, R ± 0.03 Å,$\triangle\sigma^2$ ± 30%, $\triangle E_o$ ± 20%. Each catalyst had been onstream for 22 h; reaction conditions are as stated in the text. The △k and △R ranges used in the EXAFS analysis procedures are 3.5–12.9 $Å^{-1}$ and 0.7–3.6 Å respectively.

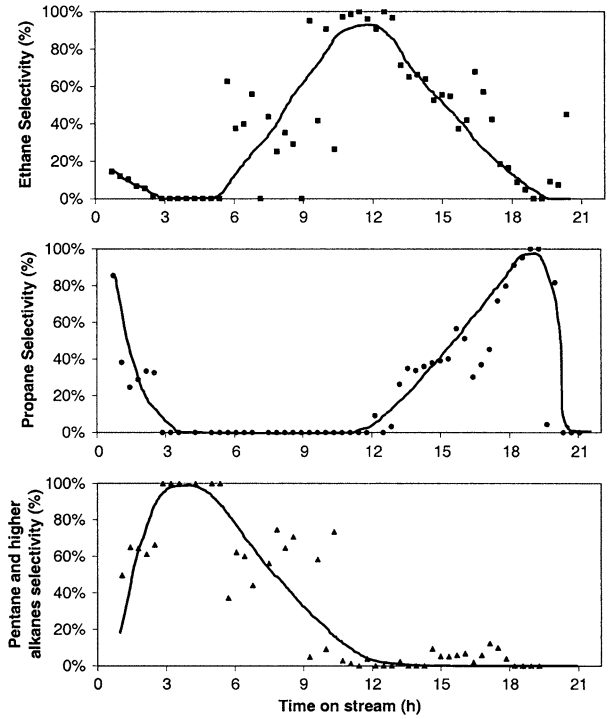

Figure 3. Change in selectivity with time on stream during methane conversion to ethane, propane, pentane, and higher alkanes. A 500-mg catalyst sample containing 1.2 wt% Ta was pretreated in H_2, at 523 K for 20 h; the reaction conditions were as follows: 1 bar, 523 K, 6.5 mL/min total flow rate of feed containing 4.9 mol% methane and 2.2 mo1% *n*-butane in helium.

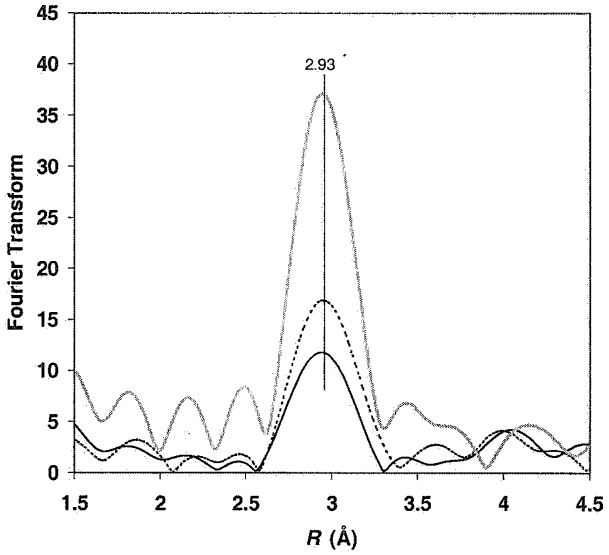

Figure 4. Magnitude of the k^3-weighted Fourier transform of the experimental EXAFS spectra characterizing the unused catalyst samples treated at 523 (solid black line), 623 (dotted line), and 723 K (gray line), with all contributions except the Ta–Ta contribution subtracted from each overall spectrum. The spectra were phase- and amplitude-corrected for Ta.

Ta–Ta coordination number increased, suggesting that the clusters grew parallel to the SiO_2 surface and not perpendicular to it [11]. The cluster diameters were calculated from models constructed by assuming a monolayer of hexagonally close-packed Ta atoms. Atoms were added to the model cluster until the weighted average Ta–Ta coordination number matched the EXAFS-derived Ta–Ta coordination number.

The overall k^3-weighted EXAFS data, the k^1-weighted Fourier transform of the data, the k^3-weighted Fourier transform of the data, and their respective fits for the used catalyst samples that had been pretreated in H_2 at 523 and 623 K are shown in figures 5 and 6. The EXAFS spectra of the used catalysts again demonstrate the presence of clusters, indicated by the Ta–Ta contributions in the phase and amplitude-corrected Fourier transforms at 3.08 and at 3.10 Å, characteristic of the samples pretreated at 523 and 623 K, respectively (figure 7a, b). These Ta–Ta distances are longer than the Ta–Ta distance of 2.93 Å found for the freshly treated samples. Because the used treated catalyst was charac-

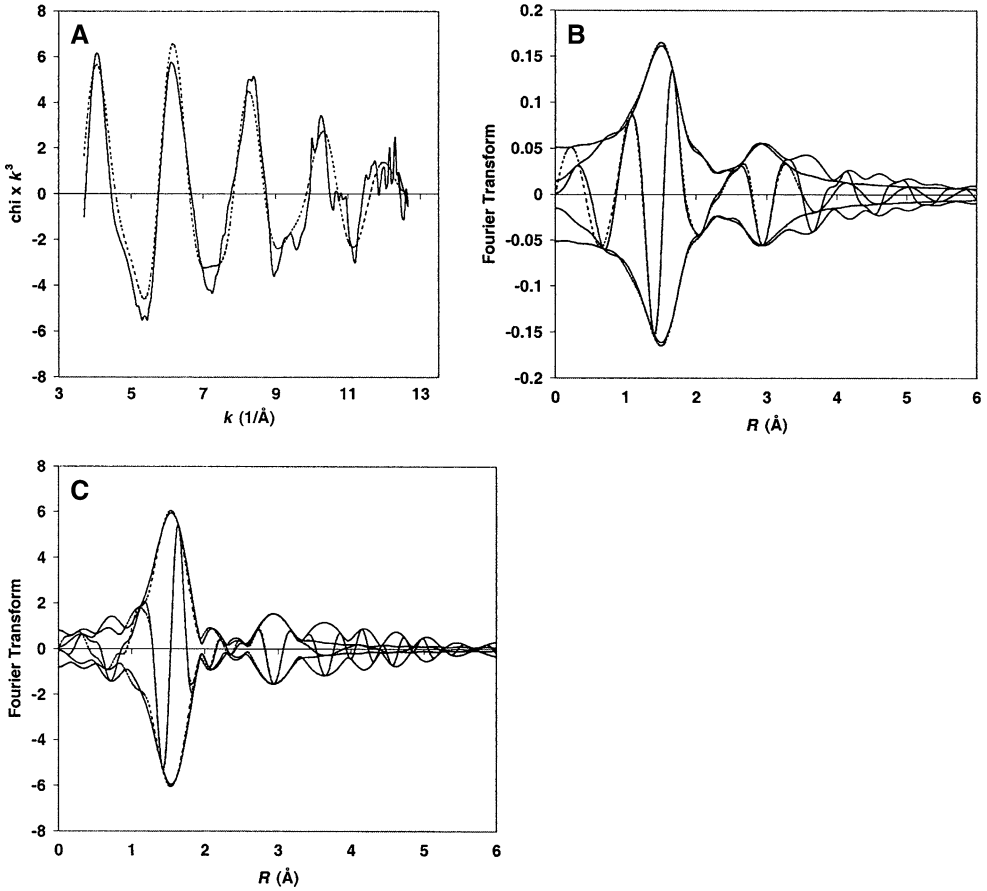

Figure 5. k^3-weighted EXAFS data (A, solid line), magnitude and imaginary part of the k^1-weighted Fourier transform of the data (B, solid line), and the magnitude and imaginary part of the k^3-weighted Fourier transform (C, solid line) of the data and their respective fits (dotted lines in A, B, and C) characterizing the used catalyst sample that had been pretreated in H_2 at 523 K. The catalysts had been onstream for 22 h; reaction conditions are stated in the text.

terized by Ta–Ta bonds that are approximately 0.17 Å longer than those characterizing the freshly treated catalyst, we infer that the adsorption of reactants and/or subsequent catalytic reaction caused oxidation of the cluster. Although the Ta–Ta distance changed, the Ta–Ta coordination number did not change substantially as a result of contact with the reactants methane and *n*-butane in the flow reactor, indicating that the cluster nuclearity remained nearly the same in each catalyst.

The EXAFS data also indicate that the coordination number of the contribution identified as a Ta–O contribution increased from approximately 3 to approximately 4 as a result of contact with these reactants. Because all the samples were handled in the absence of air and moisture, we do not attribute the increase in the Ta–O coordination number to the presence of additional oxygen ligands on the tantalum [12]. We suggest instead that this increase may be an indication of the formation of contributions that cannot be distinguished from Ta–O contributions in the EXAFS analysis. For example, it could be evidence of the formation of Ta=C bonds. This suggestion is tentative and based on the following reasoning: The interatomic distance corresponding to the Ta–O contribution (1.90 and 1.89 Å for the samples pretreated at 52.3 and 623 K, respectively) is also consistent with the Ta=C distances determined crystallographically for a number of compounds of tantalum, including, for example, Ta(CH−*t*−Bu)[NCN](O-tBu)$_2$ (Ta=C: 1.914 Å) [13], $TaCl_2$(CH-t-Bu)(CNN) (Ta=C: 1.860 Å) [14], and Cp*Ta($CHSiMe_3$)(CH_2SiMe_3)$_2$ (Ta=C: 1.920 Å) [15] (where Bu is butyl). Thus, we suggest that Ta=C bonds might have formed by reaction of alkanes with the freshly treated catalyst [16].

4.3. Summary

The results indicate the catalytic conversion of methane in the presence of the SiO_2-supported tantalum: clusters; the catalytic activity decreased as the average cluster size increased. Each deactivated catalyst is characterized by nearly the same average number of Ta atoms per cluster as the freshly treated catalyst, but with elongated Ta–Ta bonds. The trends in selectivity did not change with the temperature used to pretreat the sample in H_2; the cluster size did not affect the catalyst selectivity significantly.

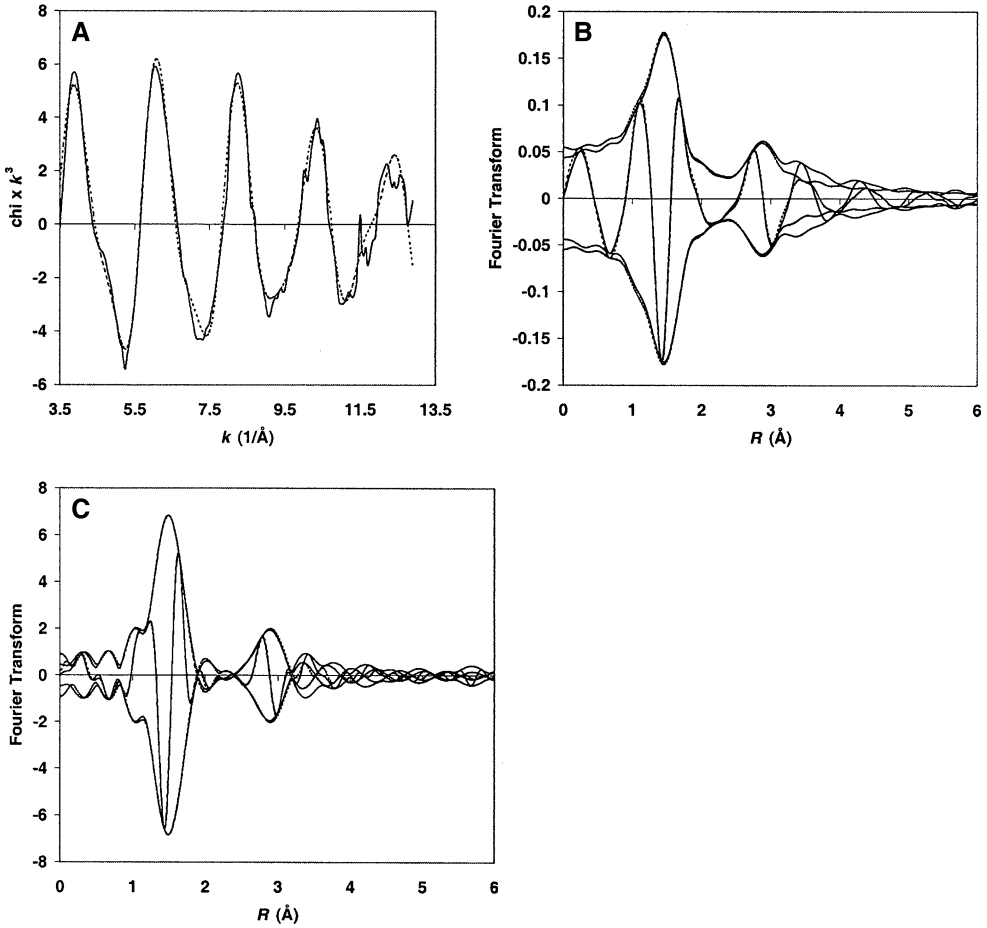

Figure 6. k^3–weighted EXAFS data (A, solid line), magnitude and imaginary part of the k^1-weighted Fourier transform of the data (B, solid line), and magnitude and imaginary part of the k^3-weighted Fourier transform (C, solid line) of the data and their respective fits (dashed lines in A, B, and C) characterizing the used catalyst sample that had been pretreated in H_2 at 623 K. The catalysts had been onstream for 22 h; reaction conditions are stated in the text.

5. Discussion

5.1. Catalyst performance

The results presented here are the first indicating the interconversion of alkalies with a supported catalyst consisting of clusters of an early transition metal. The product distribution observed when the catalyst was barely deactivated (at TOS < 4 h), consisting primarily of pentanes and propane, is consistent with the disproportionation of *n*-butane as the predominant reaction,

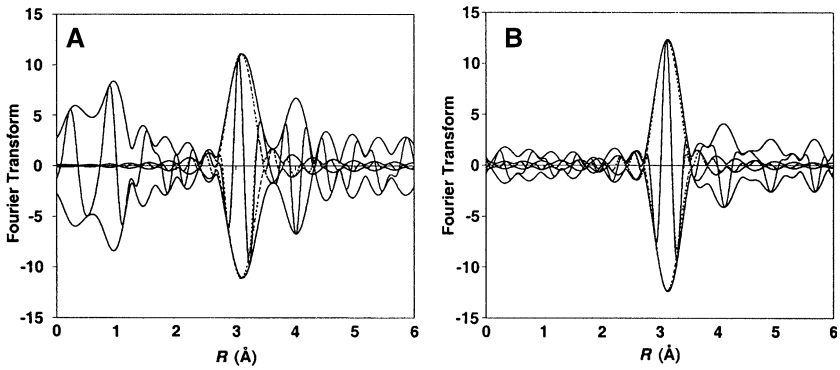

Figure 7. Magnitude and imaginary part of the phase- and amplitude-corrected k^3-weighted Fourier transform of the experimental spectra (solid line) and the fit (dotted line) characterizing the used catalysts that had been pretreated at 523 K (A) and 623 K (B) after all contributions to the EXAFS model except the Ta–Ta contribution were subtracted from the data. The catalysts had been onstream for 22 h; reaction conditions are as stated in the text.

but we infer that other reactions must have been taking place also, because the data demonstrate that methane conversion was significant.

Because of the complexity imposed by catalyst deactivation and the lack of many data at various conversions, we lack a basis for determining a quantitative reaction network. We suggest a tentative explanation of the product distribution data on the basis of literature reports.

Vidal et al. [17] demonstrated the metathesis (disproportionation) of alkanes in the presence of a SiO_2-supported tantalum catalyst prepared from $Ta(CH_2CMe_3)_3(CHCMe_3)$ (where Me is methyl). On the basis of EXAFS data, the authors concluded that the supported tantalum catalyst was a mononuclear complex anchored to the support, in contrast to our clusters. We also reported evidence of catalysis of propane disproportionation and ethane disproportionation by our SiO_2-supported tantalum clusters [18], We infer that disproportionation of *n*-butane occurred similarly.

Furthermore, Soulivong et al. [19], using essentially the same catalyst as Vidal et al. [17], observed >99% selectivity for ethane when methane reacted with propane at 523 K and a pressure of 50×10^2 kPa with a feed methane-to-propane molar ratio of 1250; this ratio is much greater than our feed molar ratio of methane to *n*-butane of approximately 2. Soulivong et al. reported results of isotopic labeling experiments showing that methane reacted with propane in a reaction they described as a cross metathesis of methane with propane (a reverse disproportionation):

$$CH_4 + C_3H_8 \longrightarrow 2C_2H_6 \qquad (1)$$

These authors did not observe significant yields of other products, presumably because of the large excess of methane over propane in their feeds.

Consistent with these literature reports [17, 18, 19], our product distribution data can be explained approximately by the disproportionation of *n*-butane accompanied by the reaction of methane with other alkanes. To account approximately for our observed products other than propane and pentane, we consider the reaction of methane to be primarily with propane and *n*-butane. Thus, a simplified reaction network is represented as including the following reactions:

$$2C_4H_{10} \longrightarrow C_3H_8 + C_5H_{12} \qquad (2)$$

and

$$CH_4 + C_4H_{10} \longrightarrow C_2H_6 + C_3H_8 \qquad (3)$$

$$CH_4 + C_3H_8 \longrightarrow 2C_2H_6 \qquad (4)$$

The occurrence of reaction (2) is evident from the predominance of propane and pentane in the product stream at TOS < 4 h. The predominance of ethane in the product at TOS $\approx$ 12 h suggests the importance of reactions (3) and (4); the high ratio of methane to the *n*-butane disproportionation products might account for its converting most of the propane formed from reactions (2) and (3) at TOS $\approx$ 12 h, consistent with the lack of observed propane in the product (the ethane selectivity was near 100%); at higher values of TOS, when catalyst had undergone more deactivation, propane was observed as a product, and its selectivity increased as the ethane selectivity decreased, consistent with the lack of complete consumption of propane produced by reactions (2) and (3). We emphasize that the statements about the reaction network are simplified; more data are required to establish this network and how it might change with catalyst deactivation.

Our data observed for TOS > 12 h indicate a further decrease in the conversion of methane with increasing TOS. On the basis of these observations, we associate changes in ethane selectivity with changes in methane conversion. The TOS for high ethane selectivity (TOS = 12 h) did not correspond to the TOS for high methane conversions (at TOS less than about 12 h), and there seems to have been an induction time (a delay in the increase in ethane selectivity) caused by some change in the catalyst; such changes are described in the following section.

5.2. Changes in catalyst during operation

Our EXAFS results indicate changes in the average Ta–Ta bond length resulting from contact of the sample with the reactants as well as changes in the average tantalum cluster size resulting from changes in the pretreatment temperature. Each is correlated with changes in the catalytic activity for methane conversion and discussed below.

We consider the correlation with the Ta–Ta bond length first: The value of 3.10 Å was observed for the used catalyst samples when the catalytic activity for methane conversion was near zero at the end of the catalytic reaction experiment. The highest catalytic activity was observed at start of each run (after H_2 treatment), when the Ta–Ta bond length was 2.93 Å. The bond length at the end of the run demonstrates an elongation of the Ta–Ta bond by approximately 0.17 Å relative to the freshly treated sample.

Changes in metal–metal bond lengths such as that reported here are indicative of changes in the oxidation state of early transition metal clusters, with longer metal–metal bonds indicating more highly oxidized clusters [20, 21, 22]. Thus, we suggest that the elongation of the Ta–Ta bond from 2.93 to 3.10 Å resulting from contacting of the freshly treated samples with the reactants represents an oxidation of the clusters—which was accompanied by a near total loss of activity for methane conversion after 22 h. Because the samples demonstrated the highest activity when the tantalum clusters were in the most highly reduced state (represented by a

Ta–Ta bond length of 2.93 Å), we suggest that maintaining the clusters in a reduced state might mitigate the loss in catalytic activity.

The second type change that is correlated with the catalytic activity is the average tantalum cluster size, indicated by the Ta–Ta coordination number. The data show that the average cluster size was controlled by the choice of pretreatment temperature; higher pretreatment temperatures gave larger clusters. Catalysts with average cluster diameters estimated to be 0.3, 0.8, and 2 nm were prepared at pretreatment temperatures of 523, 623, and 723 K, respectively. The samples containing the smallest clusters were the most active for methane conversion, and the largest were the least active.

Taken together, the two types of changes in metal–metal bonding demonstrate that catalytic activity is sensitive to changes in the distance and number of neighboring Ta atoms.

Our EXAFS results also suggest the presence of Ta = C groups in the used catalysts. These are suggested to participate in the catalytic reaction as they result from contacting of the supported clusters with the reactants. We suggest that Ta–Ta bonding influenced the Ta = C bonding as well, because the catalytic activity was near zero when the average Ta–Ta bond length was 3.10 Å. Thus, we suggest a relationship between the metal–metal bonding and metal–ligand bonding. Cotton's work gives insight into how metal–metal bonding might affect ligands bonded to group five metal clusters [20]. Cotton's group performed calculations based on theory to characterize related trinuclear clusters of $Nb_3(\mu_3{-}Cl)(\mu{-}Cl)_3\ Cl_6(PH_3)_3^-$ and $Nb_3(\mu_3{-}Cl)(\mu{-}Cl)_3Cl_3(PH_3)_6$, demonstrating that the molecular orbitals of metal–ligand bonds are of mixed character—that is, they incorporate some character of metal–metal bonding orbitals (up to approximately 15% metal-metal bonding character), as well as metal–ligand orbitals. Thus, for our supported clusters, we might expect that changes in metal–metal bonding might influence the ability of the Ta = C bond to participate in the catalytic reaction. Our results do not indicate how this might occur. We caution that this comparison with Cotton's work is limited because of differences in the identity of the metal for which the calculations were performed and differences in the type of metal–ligand bonding. Nonetheless, our results suggest opportunities to tune the surface species to minimize deactivation.

6. Conclusions

Catalysts consisting of SiO_2-supported tantalum clusters are active for the conversion of methane with *n*-butane to give ethane, propane, and pentanes; the catalytic activity decreased with increasing average cluster size in the range from about 0.3 to 2 nm in diameter. The used catalysts contained clusters of approximately the same nuclearity as the fresh catalysts. Characterization of the used catalysts by EXAFS spectroscopy indicates that the Ta–Ta bond length of the clusters in the used catalysts are greater by approximately 0.17 Å than those characterizing the clusters in the fresh catalysts; we associate the changes in Ta–Ta bond length with observed deactivation of the catalysts. The catalyst performance data are consistent with alkane disproportionation reactions and their reverse.

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[11] If the clusters had grown perpendicular to the SiO_2 surface, we would expect the Ta–O coordination number to have decreased, in contrast to the observations.
[12] As a control experiment, a sample that had been pretreated at 523 K in H_2 was exposed to air, and the EXAFS spectrum was acquired. The Ta–O coordination number was determined to be 5.4, an increase of two over the freshly treated sample. Details of this sample are given elsewhere [13].
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