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## COMMUNICATION

# The use of well-defined surface organometallic complex as a probe molecule: $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$ shows different isolated silanol sites on silica surface

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Accepted 00th January 2012Yin Chen,<sup>a</sup> Bin Zheng,<sup>a</sup> Edy Abou-Hamad,<sup>a</sup> Ali Hamieh,<sup>a</sup> Bilel Hamzaoui,<sup>a</sup> Kuo-wei Huang,<sup>a</sup> Jean-marie Basset<sup>a,\*</sup>

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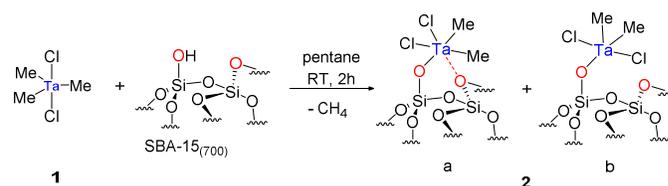
**Ta<sup>V</sup>Cl<sub>2</sub>Me<sub>3</sub> reacts with silica<sub>(700)</sub> and produces two different  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  surface organometallic species, suggesting a heterogeneity of the highly dehydroxylated silica surface, which was studied with a combined experimental and theoretical approach.**

Silica, the most abundant material on this world, has many important applications as reported by an enormous body of literature.<sup>1</sup> Amorphous silica, with a surface area varying from 10 to ca. 1000 m<sup>2</sup>/g, is a very important support of choice for the development of heterogeneous catalysts. Chemical industries generally prefer heterogeneous catalysis, but it is very difficult to develop catalysts in a non-empirical way for their complexity, which precludes their understanding at the molecular level and their development through structure reactivity relationship. Surface organometallic chemistry (SOMC) bridged the gap between the homogeneous and heterogeneous catalysis,<sup>2</sup> greatly promoted the study of heterogeneous catalysis and lead to the development of efficient single-site catalyst, in some cases the catalytic performances are better than the homogeneous equivalent,<sup>3</sup> and even unprecedented reactivity observed, such as the low temperature hydrogenolysis and metathesis of alkanes.<sup>4</sup>

A good understanding of the silica surface is extremely important for the design and synthesis of the surface organometallic compounds, to achieve better catalysis result. Generally speaking, silica is composed of tetrahedral SiO<sub>4</sub> units, and exposes siloxane bridges (Si–O–Si), and silanols (RSi–OH) as the surface terminations. Siloxane bridges can have several sizes, typically from six to ten member rings, while silanols are either geminal, vicinal or isolated.<sup>5</sup> Upon dehydroxylation treatment at high temperature under vacuum, typically 700 °C, isolated silanol groups were obtained and can be used for anchoring active reaction sites. These isolated silanols allow the preparation of so-called “single-site” heterogeneous catalysts as evidenced by spectroscopic and reactivity studies.<sup>2,3</sup>

However, in some cases the heterogeneity of the surface of silica-700 is revealed,<sup>6</sup> for example, two species have been obtained by grafting (R<sub>2</sub>N)<sub>2</sub>Mo(=CHR)(≡NAr)<sup>7</sup> or Ta(=CHtBu)(CH<sub>2</sub>tBu)<sub>3</sub><sup>8</sup> on the surface of silica<sub>(700)</sub>, Os(=CHtBu)<sub>2</sub>(CH<sub>2</sub>tBu)<sub>2</sub><sup>9</sup> partly reacts with silanols on the silica<sub>(700)</sub> surface,  $[(\equiv\text{SiO})\text{Zr}(\text{CH}_2\text{tBu})_3]/\text{Silica}_{(700)}$  generates  $[(\equiv\text{SiO})_2\text{Zr}(\text{H})_2]$  and  $[(\equiv\text{SiO})_3\text{Zr}(\text{H})]$  in the same time with

a ratio of 1:2,<sup>10</sup>  $[(\equiv\text{SiO})_2\text{Ta}^{\text{III}}\text{H}]/\text{Silica}_{(500)}$  grafted on the surface show different reactivity toward alkane metathesis,<sup>11</sup> adsorption of PMe<sub>3</sub> on well-defined silica supported Au<sup>(I)</sup> complexes yield two surface species  $[\equiv\text{SiO}\text{Au}(\text{PMe}_3)]$  and  $[\equiv\text{SiO}][^+\text{Au}(\text{PMe}_3)_2]$ .<sup>12</sup> These many examples indicate that the heterogeneity of the highly dehydroxylated silica surfaces may be due to the fact that silanols are surrounded by different numbers of highly or less strained Si–O–Si bridges. That is particularly evident for a metal center bonded to the silica surface via several Si–O–M bonds.<sup>6</sup> Nowadays, despite several experimental and theoretical advances in this area,<sup>5a,13</sup> it is still difficult to obtain a true picture of the surface. Here we show a surface organometallic species grafted on the silica<sub>(700)</sub>, which plays the role as a probe for the surface silanols heterogeneity. Recently, in the preparation of the surface tantalum species  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  (Scheme 1),<sup>14</sup> two species with different mobility on the silica surface were produced and identified by SS-NMR. The major species **2a** has less mobility than the minor species **2b**, which was supposed to be due to the coordination of the surface oxygen (See Support information).

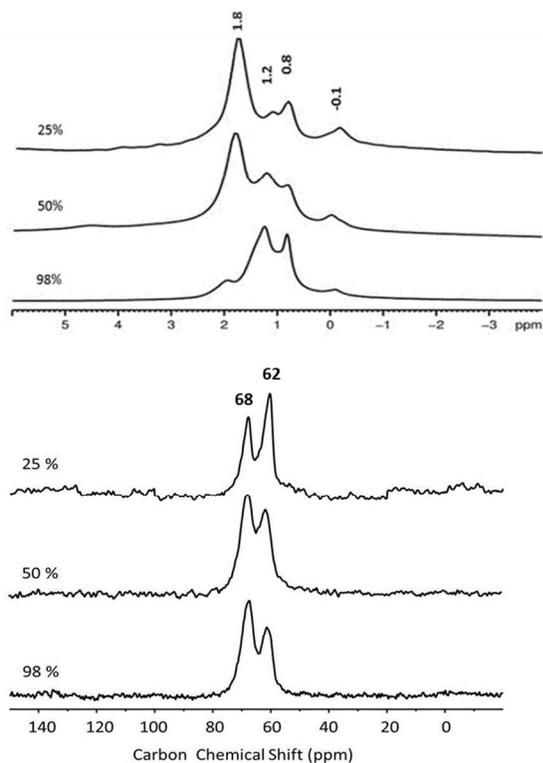


**Scheme 1.** Synthesis of  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$

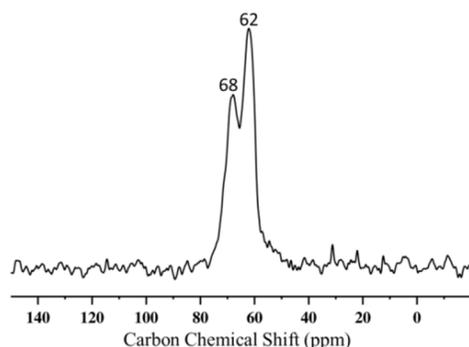
In the present study, we found the surface species  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  is helpful to understand the heterogeneity of the silanols on the surface of silica<sub>(700)</sub>. Generally, NMR results show  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  species **2a** and **2b** give carbon signals at 68, 62 ppm and corresponding proton signals at 1.2, 0.8 ppm respectively. Elemental analysis, mass balance, systematical SS-NMR experiments confirmed the structure of the surface species as  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$ <sup>14</sup> (see support information).

Using a more detailed approach, we found the silanols on the surface have different reactivity toward the precursor Ta<sup>V</sup>Cl<sub>2</sub>Me<sub>3</sub>. By grafting varying amounts of TaCl<sub>2</sub>(<sup>13</sup>CH<sub>3</sub>)<sub>3</sub> per silica surface silanol (25/50/98 Ta/Si–OH (mol%)), <sup>1</sup>H-NMR and <sup>13</sup>C-NMR experiment

results show the ratio of **2a/2b** varies significantly (Figure. 1, S5) with increasing precursor overload. At low loading of the precursor with low coverage of the silica surface, **2a** is the major species, while **2b** becomes the major species at higher loading.



**Figure 1:** up:  $^1\text{H}$  MAS NMR, down:  $^{13}\text{C}$  CP/MAS NMR spectra of  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]/\text{SBA-15}_{(700)}$  at with 25%, 50% and 98% coverage of the surface silanols

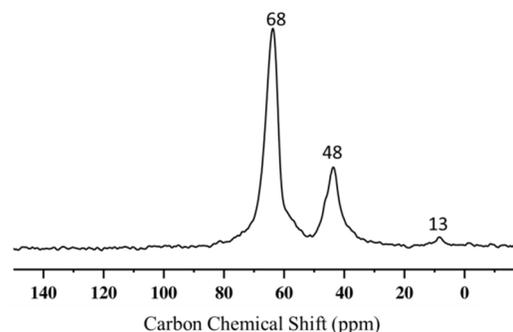


**Figure 2:**  $^{13}\text{C}$  CP/MAS NMR of  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  synthesized at  $-40\text{ }^\circ\text{C}$

When the grafting reaction was performed at  $-40\text{ }^\circ\text{C}$  with short reaction time (10 min), the  $^{13}\text{C}$ -NMR result shows that **2b** was also produced as the major product (Figure 2). These results identify the isolated silanols on the surface have different reactivity towards the precursor.

When  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]/\text{Aerosil}_{(700)}$  was treated with  $\text{NEt}_3$ , SS-NMR shows the chemical shift of **2a** was not influenced by this treatment, but the chemical shift of **2b** shifted to high-field from 62 ppm to 48 ppm (Figure 3), indicating a coordination of the Lewis base  $\text{NEt}_3$  to **2b**. Elemental analysis showed only around 0.5 equiv. of  $\text{NEt}_3$  is absorbed compare to the amount of Ta grafted on the

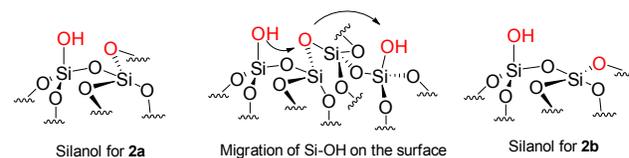
surface (Figure S6, 7). Obviously, Si-O-Si bridge adjacent to the surface species **2a** makes one kind of surface chelate with the sigma siloxy bond, the tantalum becoming hexa-coordinate with the strong and rigid surface chelate, and can't accommodate an incoming  $\text{NEt}_3$  ligand. This phenomenon was also found with the surface species  $[\equiv\text{SiOLn}(\text{NSiMe}_2)_2]$  ( $\text{Ln}=\text{Y, La, Nd, Sm}$ ), only 80% of this species can coordinate with an additional ligand  $\text{O}=\text{PPh}_3$ .<sup>15</sup>



**Figure 3:** The  $^{13}\text{C}$  CP/MAS NMR of  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]/\text{Aerosil}_{(700)}$  after treatment of  $\text{NEt}_3$ .

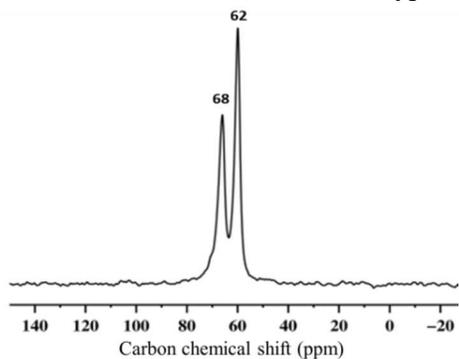
The amorphous silica has different textures and morphologies, and it is very interesting to know whether that will affect the ratio of these different species on the surface. Three different representative kinds of amorphous silica, Aerosil-200, SBA-15 and MCF (Mesocellular siliceous foams) were used as the support to prepare  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  (all these silica were dehydroxylated at  $700\text{ }^\circ\text{C}$  under  $10^{-5}$  mbar vacuum for 10 h before to use, other characterization data see SI, with a surface coverage around 98% based on IR). NMR experiment results show  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  on these different silica exhibit few difference (Figure S8, S9, Table S3), which indicates the difference of texture and morphology have limited influence on the surface silanols of silica-700.

However, we found the ratio of **2a** and **2b** on the silica surface changed a lot after the silica dehydroxylated under  $1000\text{ }^\circ\text{C}$ . When  $\text{TaCl}_2\text{Me}_3$  grafted on the  $\text{SBA-15}_{(1000)}$ , **2a** and **2b** were still produced, but the ratio decreased from 2:1 to 4:3 compare to  $\text{SBA-15}_{(700)}$  (Fig. S10). With  $\text{Aerosil}_{(1000)}$ , the ratio of **2a** and **2b** reversed (Figure 4) from 3:1 to 2:3 compare to  $\text{Aerosil}_{(700)}$ . That illustrates that these two kinds of silanols behave differently in the dehydroxylation treatment, the silanols lead to **2a** are more likely to be dehydroxylated than the other one under  $1000\text{ }^\circ\text{C}$ . Notable change was noticed for the silica texture after this treatment, different **2a/2b** ratio was found with  $\text{SBA-15}_{(1000)}$  and  $\text{Aerosil}_{(1000)}$  compare to silica-700. According to previous theoretical and experimental studies, the dehydroxylation of separated surface silanols on silica<sub>(700)</sub> involves the Si-OH migration on the surface,  $\equiv\text{Si-OH}$  reacts with the Si-O-Si bridge in the nearby and shift to the neighborhood of another  $\equiv\text{Si-OH}$  group, to produce a new Si-O-Si bridge and one molecule of  $\text{H}_2\text{O}$ . As above, the results show the silanol leading to **2a** has the Si-O-Si bridge in the near vicinity. It's reasonable to accept that the proximity will favor the surface migration of the OH and the following dehydroxylation process (scheme 2). That also coincides with what we observed in the dehydroxylation treatment.



**Scheme 2.** Different kinds of silanols on the silica surface

In order to have a detailed understanding of the structure of  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  on the silica surface and explain the observed NMR results, we performed DFT calculation on the surface species **2a** and **2b**. The optimized geometries of the species **2a** has a O-Ta...O angle at  $97.12^\circ$ , with a Ta...O coordination bond length of 2.5 Å, coincides with our previous EXAFS data result with a surface Ta...O coordination bond at 2.6 Å.<sup>16</sup> The calculated chemical shift difference between **2a** and **2b** is 5.2 ppm, while the experimental value is 6.2 ppm. Since the surface species are not equal as affected by the siloxane neighboring bridges, we try to simulate a more actual surface species by varying the O-Ta...O angle in a  $10^\circ$  plus-minus range,<sup>17</sup> and found the chemical shift difference between **2a** and **2b** is in a range of  $5.2\pm 3.0$  ppm (Figure S13). That coincides with the experimental results, and confirms the chemical shift difference of **2a** and **2b** is due to the coordination of the surface oxygen.



**Figure 4:** The  $^{13}\text{C}$  CP MAS NMR of  $(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2$  grafted on Aerosil<sub>(1000)</sub>.

**Table 2:** DFT calculated Nuclear Magnetic Shielding for carbon in **2a** and **2b**

Model System	Methyl Group No.	$\sigma_{\text{iso}}(^{13}\text{C})$ (ppm) <sup>a</sup>
2a	1	81.4
	2	64.1
	Average	72.8
2b	1	67.6
	2	67.5
	Average	67.6

a. more information see support information, chemical shift is not calibrated.

In conclusion, with a combined experimental and theoretical approach, we illustrated the heterogeneity of the silanols on the silica surface, partially dehydroxylated at  $700^\circ\text{C}$ , by using  $(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2$  as a probe species. The isolated silanols on the silica surface can be divided into two kinds as affected by the siloxane neighboring bridges. These silanols have different reactivity towards  $\text{TaCl}_2\text{Me}_3$ , and produce different surface  $(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2$  species as identified by NMR, mass balance and DFT calculation; They also behave different in the dehydroxylation treatment under  $1000^\circ\text{C}$ , while the silanols near to siloxane bridge are more likely to be dehydroxylated. These results provide a clear image for the heterogeneity of the silica surface.

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## Notes and references

<sup>a</sup> King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia. E-mail: jeanmarie.basset@kaust.edu.sa

† Electronic supplementary information (ESI) available: General procedures, experimental details and additional characterization data. See DOI: 10.1039/XXXXXX

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