Operando infrared spectroscopy evidence of formation hydrosiliconate anion during the interaction between triethoxysilane and hydroxyl-containing anion-exchange resins

D A Makarov, A V Vorotyntsev, A N Petukhov, and A N Markov
Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Nizhny Novgorod, Russian Federation, 603950

Abstract. The in situ study of the interaction between triethoxysilane and a free hydroxyl anion-containing anion-exchange resin using the FTIR spectroscopy method showed the formation of the pentacoordinated silicon-containing anion, namely trialkoxyhydroxyhydrosiliconate anion. In the present work, the SiH and SiOH group bands of the formed hydrosiliconate anion are assigned. The ethylmethylketone reduction by triethoxysilane in the presence of the free hydroxyl anion-containing anion exchange resin was found to give an alcohol-derived product. The changes in the FTIR spectra recorded in situ that are taking place during the reduction are discussed.

1. Introduction
As the production of microelectronics and solar cells grows, the need for high purity silicon is continuing to grow as well. At this moment, the most of polycrystalline silicon is produced via the Siemens process and its modifications. The Siemens process has certain disadvantages i.e. high cost of the product, high energy consumption (about 100kWh/kg) due to high temperatures (850 – 1000 °C) used, it yields to very toxic and corrosive compounds (SiCl4, HCl, Cl2), the process is very slow (about 1kg/h) [1,2]. The main alternative to the Siemens process is the Union Carbide process. The main idea of the later is to obtain polysilicon via thermal decomposition of monosilane obtained by dismutation of trichlorosilane catalyzed by ion-exchange resins containing quaternary ammonium groups. The advantages of this process are low temperatures (80 °C) and thus low energy consumption, a higher level of safety for personal and environment [3]. Silane can be obtained not only by disproportionation of trichlorosilane but also by catalytic dismutation of triethoxysilane (TES). This process gives such advantages over the previous one as the ease of separation (silane is the only gaseous product of the reaction), the safety (TES and tetraethoxysilane are much less volatile and toxic than their chloro analogues), the simplicity of the reaction apparatus construction (there is no need for rectification column, recycle system other than a simple condenser).

Anion-exchange resins are promising candidates to TES disproportionation catalysts as they can be easily separated from the reaction mixture. At the present moment, there are only a few studies concerning disproportionation of TES over different catalysts [4,5,6] and, to our best knowledge, there are only two works concerning TES dismutation over anion-exchange resins [5,7]. All these studies are accented on the yield of the reaction and the conversion of initial TES while the mechanism is guessed based on works regarding penta and hexacoordinated silicon complexes [8]. Understanding of
the reaction mechanism may be crucial to design active and efficient catalyst. The present work is devoted to study TES interaction with an anion-exchange resin catalyst in situ.

2. Experimental

2.1. Materials
Anion-exchange resin TOKEM 320 OH-form was purchased from TOKEM Company (Russia). Butanone-2 (ethylmethylketone, MEK) was generously provided by E. V. Galisevich. TES was purchased from Sigma Aldrich (Germany).

2.2. Catalyst preparation and spectra acquisition
The sample of anion-exchange resin was dried in vacuo for 2 days, then dried in the nitrogen flow for 4 hours (both at room temperature), carefully ground in a mortar to give a homogenous fine powder. The powder was placed onto defatted aluminium foil used as an underlying mirror to form a very thin layer and the foil was transferred into the diffuse reflection accessory chamber. The chamber was evacuated via a vacuum pump until no changes in the sample spectrum monitored in real time were noted. The spectrum of the sample layered on the aluminium foil was used as a background spectrum. TES was supplied into the chamber in a gaseous form from an evacuated glass vile. After the equilibrium was achieved, the spectrum of the sample exposed to the TES vapours was recorded. The spectrum of neat TES was obtained the same way excluding the presence of the catalyst (i.e. on the naked foil). All spectra were recorded on IRTracer-100 (Shimadzu, Japan) equipped with MCT detector (Shimadzu, Japan; signal/noise ratio 8000:1, measurement range of 5000 to 650 cm⁻¹) and diffuse reflection accessory DiffusIR (PIKE, US) with 2 cm⁻¹ resolution and 2.8 mirror speed using LabSolutions IR (Shimadzu, Japan) software.

2.3. Reduction of MEK by TES in the presence of anion-exchange resin
To study the interaction between MEK and TES in the presence of the TOKEM 320 OH-form anion-exchange resin MEK was supplied into the FTIR chamber after the equilibrium between TES and the catalyst was achieved and then the chamber was sealed. The spectrum of the thin layer of the catalyst placed onto the aluminium foil spectrum was used again as a background. Spectra of the system were recorded for 2.5 hours until the reaction rate dropped significantly and only minor changes in the spectrum could be noted. The neat MEK spectrum was obtained the same way as the TES one.

3. Results and discussion

3.1. Interaction between TES and anion-exchange resin
TOKEM 320 OH-form anion-exchange resin contains free hydroxyl anions and quaternary ammonium cations chemically linked to the polymer matrix. It could be assumed that hydroxyl-containing substance may react with TES by three different pathways described by the following equations:

\[(EtO)_3SiH + H_2O \overset{\text{cat}}{\rightarrow} H_2 + (EtO)_3SiOH\]  \hspace{1cm} (1.a)
\[2(EtO)_3SiOH \rightarrow H_2O + ((EtO)_3SiO)_2\]  \hspace{1cm} (1.b)
\[(EtO)_3SiX + H_2O \overset{\text{cat}}{\rightarrow} EtOH + (EtO)_{2}SiX(OH)\ (X = OH \ or \ H)\]  \hspace{1cm} (1.c)
\[(EtO)_3SiH + OH^- \rightarrow H_2O + (EtO)_3Si^-\]  \hspace{1cm} (2)
\[(EtO)_3SiH + OH^- \rightarrow [(EtO)_3(OH)Si]^-\]  \hspace{1cm} (3)

The first three equations (1.a-c) describe the oxidation of the SiH bond by the residual water, the condensation of the released silanol and the hydrolysis of the silanol or silane. These processes are well described in works [9, 10, 11]. Acid-base interaction between TES and the catalyst leading to triethoxysilyl anion and water as a by-product is described by the equation (2). Such behaviour is common for trichlorosilane and was studied in detail by R. Benkeser [12]. Finally, the nucleophilic attack of the hydroxyl anion on silicon atom leading to the formation of the pentacoordinated
hydrosiliconate anion is shown in the equation (3). The formation of pentacoordinated siliconates is described in works by Corriu et. al. [8, 13].

![Figure 1. FTIR spectra of neat TES and interaction between TES and TOKEM 320 OH-form anion-exchange resin (graphics are shifted along the y-axis for clarity).](image)

TES reacts with the powdered catalyst quite rapidly and the change in the FTIR spectrum occurred over several minutes. As it can be seen from figure 1, neither oxidation of SiH bond nor hydrolysis and condensation occurred. The former would lead to diminishing of the SiH band at 2202 cm\(^{-1}\) but it can be clearly seen that this band shifted to 2235 cm\(^{-1}\) due to the undergoing reaction between TES and the catalyst. The later would lead to evolution of ethanol and water but no traces of both can be noted as peaks in the OH stretching region, namely the broad peak near 3430 cm\(^{-1}\) and more narrow peak at 3640 cm\(^{-1}\), diminished. The rise of the peak at 2235 cm\(^{-1}\) also evidences against the formation of silyl anion as in that case the SiH bond band should have vanished. Several facts prove the formation of pentacoordinated hydrosiliconates in this system. As it is expected, vibration bands of the SiH \( (2202 \text{ cm}^{-1}) \) and SiOC \( (1088 \text{ cm}^{-1}) \) bonds shifted (to 2235 and 1062 cm\(^{-1}\) respectively). The diminishing of the OH stretching band evidences that hydroxyl groups of the catalysts take part in the reaction but it is expected for hydroxyl-containing silicon derivatives to also absorb infrared radiation in the 3200 – 3600 cm\(^{-1}\) region due to OH stretching [14]. Nevertheless, the presence of the OH group in the formed species can be confirmed by the presence of the bands at 785 and 844 cm\(^{-1}\) that can be attributed to the SiO stretching vibrations and bend of the SiOH group [15]. Thereby, the species forming due to the reaction between TES and TOKEM 320 OH-form anion-exchange resin contain a hydrogen atom, a hydroxyl group and do not lose any of the ethoxy groups. On the base of presented data, it can be assumed that pentacoordinate hydrosiliconate anions, namely triethoxyhydroxyhydrosiliconate \((\text{EtO})_3(\text{OH})\text{SiH}^-\) anions, formed as a result of the reaction.

3.2. Reduction of MEK by TES in the presence of anion-exchange resin

To provide further evidence of the formation of hydrosilicate species, the interaction between the TES – anion-exchange resin system and MEK was studied as pentacoordinated hydrosiliconates are known as mild reducing agents that allow to reduce ketones to corresponding secondary alcohols [16]. The reduction between TES and ketones does not proceed without catalysts like an acid-base catalyst or transition metals. The trichlorosilane – tertiary ammine system which gives trychlorosilyl anion also
reacts with ketones to give trichlorosilyl-substituted alkanes [12]. Thereby, if triethoxysilyl anions are being formed in the reaction system, ketones are expected to be reduced to triethoxylilylalkanes. Finally, compounds that do not contain SiH bond (silanols, siloxanes) do not reduce ketones. Thereby, this reaction allows to confirm or deny the presence of hydrosiliconate anions in the reaction system.

**Figure 2.** FTIR spectra of neat TES and MEK, the reaction system right after the moment MEK was supplied and 2.5 h after this moment (graphics are shifted along the y-axis for clarity).

At the start of the reaction, there is no significant difference between the spectrum of the TES – catalyst system and the TES – catalyst – MEK system except, of course, the presence of MEK bands (see figure 2). After 2 hours and 20 minutes, notable changes occurred. The intensity of the doublet with center at 1739 cm\(^{-1}\) which can be easily assigned to carbonyl group stretching vibration decreased significantly while the intensity of the band at 1167 cm\(^{-1}\) did not change much. Therefore, it can be assumed that MEK indeed reacted. The SiH band at 2202 cm\(^{-1}\) diminished and the intensity of the band at 2235 cm\(^{-1}\) also significantly decreased which means that TES also took part in the reaction. As bands that can be assigned to C-C skeletal vibrations (1009 cm\(^{-1}\)) and methyne CH stretching (2890 cm\(^{-1}\)) rose it can be concluded that MEK was reduced to the derivative of alkane or alcohol.

To discern two possible products of the reaction, namely 2-triethoxysilylbutan and butyl-2-oxytriethoxyhydroxysiliconate (see figure 3), it is tenable to look on the SiOC, SiOH and SiC band regions. The region of the 1030-1180 cm\(^{-1}\) became overcrowded but some important observations can be made. First of all, new band papered at 1040 cm\(^{-1}\) and it can be associated with the formation of the new SiOC group as it places too far from original SiOEt bands triplet (1164, 1114 and 1088 cm\(^{-1}\)) to be attributed to SiOEt group vibrations and nothing else can arouse in that region. The second point to mention is the absence of the band in the 1210-1190 cm\(^{-1}\) region that should arouse in the case of silyl-substituted alkanes [17]. And the third point is the increase in the absorbance of the bands that can be attributed to the SiOH group, namely the bands at 792 and 847 cm\(^{-1}\). The later became much more pronounced. In addition, a broad band in the OH stretching region appeared at 3250 cm\(^{-1}\). As the decrease in the absorbance in the OH stretching region due to interaction between TES and the catalyst had a maximum in a different position (3358 cm\(^{-1}\)) it can be assumed that hydroxyl group formed as a
product of the reaction between TES and MEK is not of the same nature as the hydroxyl group that reacted with TES. Thereby, it can be concluded that butyl-2-oxytriethoxyhydroxysiliconate anion is formed during the reaction between TES and MEK in the presence of TOKEM 320 OH-form anion-exchange resin.

4. Conclusion
The interaction between TES and free hydroxyl anion-containing anion exchange resin was studied using the FTIR spectroscopy method. Based on the obtained data it was concluded the named species react to give a hydrosiliconate anion as a product. This conclusion was verified by studying the reduction of MEK by TES in the presence of the anion-exchange resin and it was found MET to be reduced to a derivative of the alcohol. It was proved that anion-exchange resins can be used to catalyze the reduction of ketones by TES.

Acknowledgments
The reported study was financially supported by Russian Foundation of Basic Research (project No. 18-33-00914).

5. References
[1] Braga A F B, Moreira S P, Zampieri P R, Bacchin J M G and Mei P R 2008 Sol. Energy Mat. Sol. Cells 92 418–24
[2] Xakalashe B S and Tangstad M 2011 South. Afr. Pyromet. 2011 Int. Conf. (Johannesburg: Southern African Institute of Mining and Metallurgy) p 83
[3] Ciftja A, Engh T A and Tangstad M 2008 Refining and Recycling of Silicon: A Review (Trondheim: Norwegian University of Science and Technology)
[4] Suzuki E, Nomoto Y, Okamoto M and Ono Y 1998 Appl. Catal. A 167 7
[5] Imaki N, Haji A and Misu Y 1987 US Patent 4,667,047
[6] Parshin L N, Oparina L A, Khil’ko M Y and Trofimov B A 2003 J. Organomet. Chem. 665 246
[7] Chigondo F and Watts P 2016 Catal. Let. 146 1445–8
[8] Chuit C, Courriu R J P, Reye C and Young J C 1993 Chem. Rev. 93 1271–448
[9] Benkeser R A 1971 Acc. Chem. Res. 4 94–100
[10] Schmidt H, Scholze H and Kaiser A 1984 J. Non-Cryst. Sol. 63 1–11
[11] Benkeser R A 1971 Acc. Chem. Res. 4 94–100
[12] Brefort J-L, Courriu R J P, Guerin C, Henner B J L and Wong Chi Man W W C 1990 Organomet. 34 2378–85
[13] Griffith G W 1984 Ind. Eng. Chem. Prod. Res. Dev. 23 590–3
[15] Ignatyev I S, Partal F, Gonzalez J J L and Sundius T 2004 Spectroch. Acta A 60 1169–78
[16] LaRonde F J and Brook M A 1999 Tetrahedron Lett. 40 3507–10
[17] Arkles B and Larson G L 2013 Silicon Compounds: Silanes & Silicones (Morrisville: Gelest Inc.)