Active catalysts prepared using a vanadium-containing oligosilsesquioxane for selective photo-assisted oxidation of methane into methanal

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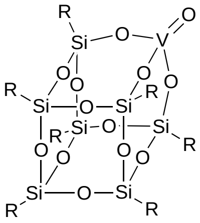
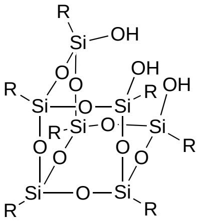
Catalysts of characteristic pore structure derived from silica-supported vanadium-containing silsesquioxane show excellent activity towards the selective photo-assisted catalytic oxidation of methane into methanal (at 493 K, 139 μmol h^{-1}, TON *ca.* 9 h^{-1}, selectivity 81%), indicating its potent abilities as an excellent precursor for porous oxide catalysts.

Supported vanadium oxide catalysts are very important in the chemical industry, especially for the selective oxidation of hydrocarbons.[1] We have reported the excellent activities of silica-supported vanadium oxide catalysts towards the selective photo-assisted catalytic oxidation of methane, ethane and propane at relatively high temperature into the corresponding aldehydes.[2] Only highly dispersed, isolated tetrahedral VO_4 species were considered to be active species, and the reactions were quite sensitive to the state of the surface. However, strict control of the surface structure is generally quite difficult.[3] Thus the development of novel methods for the preparation of catalysts which have well ordered surface species is desirable.

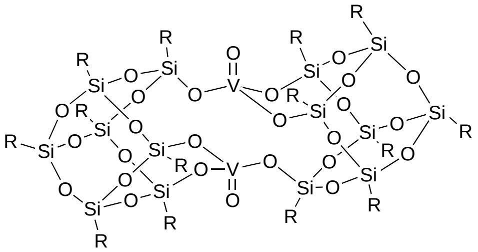
On the other hand, oligometallasilsesquioxanes such as compound **1a** have attracted attention from the viewpoint of well defined, homogeneous models for surface active sites of supported catalysts or metal-containing zeolites.[4] The catalytic activities of these oligometallasilsesquioxanes, however, have been mainly focused on alkene polymerization and metathesis. Their activities for other reactions were not well investigated.[5] It should be noted that the activity of a titanium-containing silsesquioxane towards the epoxidation of alkenes was recently reported.[6]



1a (R = c-C_6H_{11})
b (R = c-C_5H_9)



2b (R = c-C_5H_9)



3b (R = c-C_5H_9)

From the background described above, we have reported the fair to excellent activity of a vanadium-containing silsesquioxane **1b**, a cyclopentyl derivative of **1a**, for the photooxidation of benzene and cyclohexane, indicating its ability as a homogeneous analog of silica-supported catalysts.[7] Here, in order to investigate the possibility of **1b** as a precursor for heterogeneous catalysts, we prepared supported **1b**-based catalysts, and found that thermal treatment of the catalysts induces high activities towards the selective photo-assisted catalytic oxidation of methane into methanal.

Preparation of a vanadium-containing silsesquioxane **1b** was based on the procedure reported by Feher *et al.*[5a] The reaction of vanadyl triisopropoxide with incompletely condensed silsesquioxane **2b**, which was prepared by the hydrolytic condensation of cyclopentyltrichlorosilane, gave a white powder of dimer **3b** in 44% yield.[5a,7] The resultant product exists as a monomer **1b** in organic solutions at above room temperature. **1b** shows an absorption at *ca.* 252 nm in cyclohexane solution (ε = 4840 dm^3 mol^{-1} cm^{-1}). The silica-supported catalysts were prepared by incipient wetness impregnation from a pentane solution of **1b** using silica (Alfa, evacuated at 423 K for 2 h, mass ratio **1b** : silica = 1 : 3, V 1.9 mol%). The vacuum dried catalyst was designated **A**. We also prepared catalysts **B** and **C** by air-flow treatment (20 cm^3 min^{-1}) for 2 h at 523 and 723 K, respectively. It should be noted that heat treatment of **3b** without silica support often produced non-porous glassy materials.

The reaction was performed by using an upstream flow fixed-bed reactor made of silica glass. The catalyst was mounted in a flat cell (10 × 20 mm, inner thickness 1.5 mm), and covered by another silica glass tube. UV irradiation was performed from the outer side of the reactor using a 200 W high-pressure mercury lamp with a water filter. Details of the reaction apparatus were described elsewhere.[2] Chemical actinometry using iron(III) ammonium oxalate revealed that the number of photons irradiated into the catalyst bed is 6.6×10^{-7} einstein s^{-1} (250–500 nm, 1.6×10^{-7} einstein s^{-1} for 250–300 nm).

Liquid and gaseous products were collected in cold traps and gas sampling bags, respectively, followed by analysis using gas chromatography, GC–MS and ^{1}H NMR spectroscopy.

Silica-supported vanadium-containing silsesquioxane-based catalysts showed fair to excellent activities for photooxidation of methane into methanal [eqn. (1); see Table 1] and results are shown in Table 1. Preliminary experiments showed that catalyst

Table 1 Photo-assisted catalytic oxidation of methane[a]

$$CH_4 + O_2 \xrightarrow[\text{493 K, [cat.]}]{h\nu} HCHO + H_2O \qquad (1)$$

		Yield/μmol h^{-1}		
Run	Catalyst	HCHO	CO	CO_2
1	None	0	0	0
2	**B**	7.2	9	18
3	**C**	139	26	6
4	V_2O_5/SiO_2[b]	61	13	7

[a] Typical reaction conditions: amount of catalyst 50 mg, molar ratio methane : O_2 : He = 12 : 1 : 11, total gas flow rate 20 cm^3 min^{-1}, reaction temperature 493 K, reaction time 1 h.

A afforded very small amounts of the products. The result without catalyst shown in run 1 exhibits the absence of the photo-chemical reaction of methane. Control experiments without alkanes afforded none of the products, eliminating the contribution by the oxidation of organic groups of the silsesquioxane moiety. Reaction using silica support also did not afford the products.

The reaction using catalyst **C**, calcined in air at 723 K, produced methanal in a yield of 139 μmol h^{-1} (0.56% of fed methane) with the selectivity of $>80\%$. Turnover frequency for the formation of methanal was *ca.* 9 h^{-1}. Only a trace amount of methanal was formed by the reaction at *ca.* 300 K, indicating the necessity of a reaction temperature as high as 493 K. Reaction without UV irradiation did not proceed at all. For comparison, we examined the performance of a silica-supported vanadium oxide catalyst prepared by evaporation-to-dryness impregnation using ammonium metavanadate, which showed the highest activity in the previous study.[2] However, it gave only 61 μmol h^{-1} of methanal under the same reaction conditions, indicating the excellence of catalyst **C**. It should be noted that catalyst **B** including organic substituents (*vide infra*) also produced methanal, but the yield and the selectivity were low. This probably indicates the difference of the activity between the surface vanadium species on silica and that on the silsesquioxane moiety.

Then we investigated various properties of the supported catalysts. The XPS spectra of the catalysts **A** and **B** showed almost the same ratio of C 1s, corresponding to organic substituents of the silsesquioxane moiety, to Si 2p, indicating the absence of oxidation of organic substituents by treatment at 523 K in air. On the other hand, catalyst **C** was found to consist of oxides, since only trace amounts of carbonaceous materials were detected on the surface of catalyst **C**. While the BET surface area of original silica support was 259 m^2 g^{-1}, those of catalyst **A** (180 m^2 g^{-1}) and **B** (171 m^2 g^{-1}) were smaller. On the other hand, catalyst **C** had a larger surface area (349 m^2 g^{-1}). Fig. 1 shows the pore size distribution of the catalysts estimated from the desorption isotherm of nitrogen at 77 K by Dollimore–Heal method. It should be noted that the catalyst **C** was more rich in mesopores around 30 Å than the parent silica support. These characteristic features indicate the possibility of oligometalla-silsesquioxanes as novel precursors for porous oxide materials.

In conclusion, we have shown fair to excellent activities of the heterogeneous catalysts prepared using a vanadium-containing silsesquioxane **1b** for the selective photo-assisted oxidation of methane into methanal. The present results indicate the possibility of oligometallasilsesquioxanes as excellent precursors for porous oxide catalysts. We are now investigating not only the detailed structure, but also the shape selectivity of the supported catalysts.

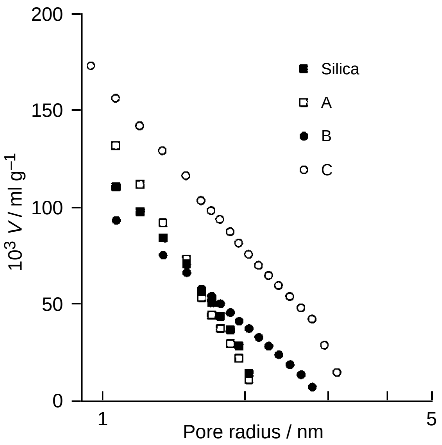


Fig. 1 Pore size distribution of silica and supported catalysts estimated by the Dollimore–Heal method (desorption, integral data)

Footnote and References

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