Preparation of Isolated VO$_4^{3-}$ Species in Silica Framework by Alkoxy-exchange Reactions between Metal Alkoxides and Polyethylene Glycol

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Isolated VO$_4^{3-}$ species incorporated in an SiO$_2$-framework were synthesized by alkoxy-exchange reactions between Si(OEt)$_4$, V(O$_t$-Bu)$_3$O, and polyethylene glycol (PEG). Similar alkoxy-exchange rates between alkoxides of vanadium and silicon with PEG were necessary to obtain isolated VO$_4^{3-}$ species in the SiO$_2$-framework. Gel was formed during the exchange reaction occurring with heating from 50 to 160 °C, liberating ethanol and $t$-butanol, and the obtained gel was calcined in air at 600 °C. The calcined samples were characterized by N$_2$ adsorption, XRD, Raman, FT-IR, H$_2$-TPR, and NMR techniques. Adsorption-desorption isotherms of N$_2$ of the obtained samples exhibited H$_4$-type hysteresis patterns, indicating the presence of narrow neck pores. In addition, the presence of micropores was confirmed. The samples had high surface areas of approximately 1000 m$^2$/g, and isolated VO$_4^{3-}$ species were present in the SiO$_2$-framework. Oxidative dehydrogenation of ethylbenzene was performed as a test reaction, using CO$_2$ as a mild oxidant. The reaction proceeded on the isolated VO$_4^{3-}$ species in the silica framework with high ethylbenzene conversion and high selectivity for styrene.

Keywords
Alkoxy-exchange reaction, Sol-gel process, Polyethylene glycol, Isolated vanadate, Vanadium oxide

1. Introduction

Vanadium-based catalysts have high activities for the oxidative dehydrogenation (ODH) of alkanes (ethane$^{1-3}$, propane$^{4-6}$, butane$^{7-9}$, and ethylbenzene$^{10-12}$) and selective oxidation of methane$^{13}$ and methanol$^{14,15}$. Among the vanadium oxide species, isolated VO$_4^{3-}$ exhibits particularly high activity and selectivity for these reactions. Isolated VO$_4^{3-}$ species can be obtained with very low loading on support oxide materials$^{16}$ (SiO$_2$, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, and MgO). However, the resultant catalysts have very low concentrations of isolated VO$_4^{3-}$ species, so large amounts of catalyst are required to achieve high yields of the desired products. In contrast, high vanadium loading results in polyvanadate and crystalline V$_2$O$_5$ phases, which have low selectivity for the desired products, leading to complete oxidation of both the feed and products.

As an alternative to supported catalysts, isolated VO$_4^{3-}$ species can be incorporated into the MCM-41 frame structure by either direct syntheses$^{17,18}$ or by ion exchange of VO$_2^{2+}$ with the template cation in as-prepared MCM-41$^{19,20}$. Similarly, V-incorporated microporous materials, such as V-silicalite$^{21,22}$ and vanadium-incorporated aluminophosphate (VAPO-5)$^{23,24}$ have been synthesized with high dispersion of vanadium species. Vanadium-incorporated mesoporous MCM-41 or MCM-48 silica frames and microporous silicalite and VAPO-5 with low vanadium concentrations (<2 wt% of V, 0.4 mmol-V/g) have moderate selectivity for the ODH of propane (ODHP)$^{21,22,23,24}$. To avoid the combustion of propylene, we previously proposed the use of lattice oxygen of the isolated VO$_4^{3-}$ species on SiO$_2$ with moderate surface area. In this process, the use of vanadium alkoxide increases the number of isolated VO$_4^{3-}$ species on SiO$_2$, resulting in very high propylene selectivity of 88 % in ODHP$^{25}$. Such VO$_4^{3-}$-incorporated SiO$_2$ catalysts could be prepared by the alkoxy-exchange reaction of polyethylene glycol (PEG) and metal (vanadium and silicon) alkoxides followed by calcination. This procedure obtained a higher isolated VO$_4^{3-}$ concentration of 1 mmol-V/g of SiO$_2$. These catalysts exhibited very high propylene selectivities of more than 95 % in ODHP using the lattice oxygen of VO$_2$$^{26}$. Moreover, the catalyst materials contained uniform mesopores and very high surface areas reaching 1000 m$^2$/g. Before calcination, the gels

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3.65 g (16.7 mmol) of TEOS and temperatures for 1 h in N2; then the reaction mixture ionization detector (FID) gas chromatography and 160

2. 1. Materials

2. 2. Preparation of VO\textsubscript{x}-incorporated SiO\textsubscript{2} Catalysts in the Presence of PEG

VO\textsubscript{x}-incorporated SiO\textsubscript{2} catalysts were prepared by the sol-gel method: 3.65 g (16.7 mmol) of TEOS and 0.5 to 2.3 mmol of V(OR) in the presence of PEG. The gels and calcined products were characterized by various analyses, such as N\textsubscript{2} adsorption-desorption isotherm, XRD, Raman, FT-IR, H\textsubscript{2}-TPR, \textsuperscript{13}C, and \textsuperscript{29}Si CP-MAS NMR spectroscopies. The obtained material was assessed as a catalyst for the oxidative dehydrogenation of ethylbenzene (EB) using CO\textsubscript{2} as a mild oxidant\textsuperscript{27}, which found good performance for ODH of EB.

2. 3. Catalyst Characterization

N\textsubscript{2} adsorption and desorption isotherms were obtained at 77 K with a Quantachrome AUTOSORB-1. The BET surface area was calculated from the BET equation. The pore-size distribution was calculated using the adsorption and desorption branches of the isotherm and the Barrett-Joyner-Halenda (BJH) formula.

Powder X-ray diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 diffractometer with monochromatized Cu K\textalpha\textsubscript{ radiation.}

Raman spectra were obtained with a Jobin Yvon T64000 spectrometer using 532-nm diode laser excitation with a CCD detector.

Fourier transform infrared (FT-IR) spectra were obtained in the transmission mode using a KBr disk with a Shimadzu FTIR3000.

Temperature-programmed reduction (TPR) was carried out with a fixed-bed quartz reactor (10 mm i.d. × 350 mm L) equipped with an on-line quadrupole mass spectrometer (Hiden Analytical Ltd., HAL201). After placing 200 mg of the catalyst into the reactor, a gas mixture of 5 mL/min H\textsubscript{2} and 20 mL/min Ar was introduced. Before the TPR measurement, the catalyst was pretreated under 5 mL/min O\textsubscript{2} and 20 mL/min Ar flow at 450 °C for 30 min to eliminate any adsorbed H\textsubscript{2}O and to oxidize any reduced vanadium species on the catalyst. Mass spectrometry was used to obtain the parent peaks of the following four compounds, H\textsubscript{2}, H\textsubscript{2}O, CO, and CO\textsubscript{2}, within 1 s, and repeated scans were collected in a personal computer.

Solid-state magic angle and cross polarization NMR measurements were performed with a JEOL model ECA-400 with a 9.39 T field. \textsuperscript{29}Si spectra were recorded at 79.4 MHz with a pulse width of 7.0 μs using 32768 scans. \textsuperscript{13}C NMR spectra were recorded at 100.5 MHz with a pulse width of 5.5 μs using 2048 scans. Tetramethylsilane was used as an external standard.

Thermal analyses of the gel were performed at a heating rate of 10 °C/min with 10 % O\textsubscript{2} in Ar using a thermogravimetric analyzer, Mac Science model TG-DTA2000SA.

2. 4. Oxidative Dehydrogenation of Ethylbenzene

Dehydrogenation of ethylbenzene (EB) was carried out using a fixed-bed flow-type quartz reactor (4 mm i.d.) at atmospheric pressure containing 50 mg of catalyst. Details of the reaction procedure and analyses were reported previously\textsuperscript{27a}.

\begin{eqnarray}
\text{Si(OE)}_2 + V(OR)_2 + 3\text{H}_2\text{O} \rightarrow \text{Si(OH)}_2 + V(OR)/2 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_2 + V(OR)/2 \text{H}_2\text{O} + 2\text{H}_2\text{O} + \text{2EOH} + 2\text{BuOH}
\end{eqnarray}
3. Results

3.1. Alkoxy-exchange Reaction between Metal Alkoxides and PEG25

To analyze the mechanism of the alkoxy-exchange reaction of metal alkoxides (TEOS and V(OR)) with PEG25, the amounts of alcohols exchanged with PEG were measured. The relationship between the amounts of recovered alcohols (t-BuOH and EtOH) and reaction temperature is shown in Fig. 1. EtOH was generated by the alkoxy-exchange reaction of TEOS and PEG25 (reaction 2), whereas t-BuOH is generated by the reaction of V(OR) and PEG25 (reaction 3).

\[
\text{Si(OEt)}_4 + 4\text{HO}-(\text{C}_2\text{H}_4\text{O})_{25}\text{H} \rightleftharpoons \text{SiO}-(\text{C}_2\text{H}_4\text{O})_{25}\text{H} + 4\text{EtOH} \tag{2}
\]

\[
\text{V(Or-Bu)}_3\text{O} + 3\text{HO}-(\text{C}_2\text{H}_4\text{O})_{25}\text{H} \rightleftharpoons \text{V(O}-(\text{C}_2\text{H}_4\text{O})_{25}\text{H})_3\text{O} + 3\text{t-BuOH} \tag{3}
\]

At all reaction temperatures, the fraction of recovered t-BuOH was larger than that of EtOH. The right axis of the ordinate shows the amount of exchanged alcohols for each metal (Si: 4 equivalent EtOH and V: 3 equivalent t-BuOH). After the reaction was carried out at 160°C for 1 h, the reaction mixture was treated under reduced pressure, and 3.0 mol EtOH and 2.7 mol t-BuOH were recovered from 1 mol of TEOS and 1 mol of V(OR), respectively. These amounts correspond to 3/4 of the ethoxy groups in TEOS and 9/10 of the butoxy groups in V(OR). Furthermore, Fig. 1 indicates that the rates of the alkoxy-exchange reactions decreased after exchanges of two EtOH and two t-BuOH equivalents in TEOS and V(OR), respectively.

Alkoxy-exchange reactions of binary systems containing V(OR) and PEG25 or TEOS and PEG25 were carried out similarly, as shown in Fig. 2. The reaction of V(OR) and PEG25 proceeded to nearly 90% ex-

change of the –OR group below 115°C, whereas TEOS did not react with PEG25 even at a higher reaction temperature of 160°C.

3.2. Catalyst Characterization

3.2.1. N₂ Adsorption and Desorption

The effects of DP of PEGx on the N₂ adsorption-desorption isotherms and BJH pore-size distributions of V(1.0)-PEGx are shown in Figs. 3(1) and 3(2), respectively. All samples exhibited IUPAC type IV isotherms with an H₃-type hysteresis loop. The amount of N₂ adsorbed at a low relative pressure \( p/p_0 < 0.1 \) was quite large, indicating the presence of micropores. The most characteristic feature of the hysteresis patterns was observed in the high \( p/p_0 \) region, with adsorption increasing at very high \( p/p_0 \). In contrast, desorption was observed in the relatively low \( p/p_0 \) region. Such a hysteresis pattern was not observed for MCM-41, MCM-48, or SBA-15 type mesopores. The pore-size distribution profiles obtained from the adsorption branches of the isotherms indicated different pore-size
distribution patterns. The peak of the pore-size distribution from the adsorption branch calculated by the BJH method changed from 1.0-2.0 to 4.0 nm with higher DP of PEG from 2 to 50.

We previously reported the specific surface area (SA), total pore volume (TPV), and average pore diameter (APD) of V-PEGx in Table 1 of ref. 26. APD was determined from the isotherms using the BJH method. With higher DP of PEGx from 2 to 50, the SA and TPV of V(1.0)-PEGx series increased from 352 to 978 m²/g and 0.24 to 0.93 mL/g, respectively, except for V(1.0)-PEG50 (944 m²/g). Therefore, the specific surface area could be controlled by the DP of PEGx.

Figures 4(1) and 4(2) show the N₂ adsorption-desorption isotherms and BJH pore-size distributions of V-PEG25 with different vanadium loadings (0.5-2.3 mmol). The samples containing 1.0 to 2.0 mmol of VOₓ exhibited similar isotherms, as described above (type IV isotherms with an H₄-type hysteresis loop). In contrast, the N₂ adsorption profile of V(2.3)-PEG25 was quite different, as N₂ adsorption drastically increased only in the very high relative pressure region (p/p₀ > 0.9), indicating adsorption by macropores. The pore-size distribution from the adsorption branch changed from 3.5 to above 60 nm with higher vanadium content from 1.0-2.0 to 2.3 mmol. Table 1 in ref. 26 summarizes the SA, TPV, and APD of V(0.5-2.3)-PEG25 containing different amounts of vanadium. With higher VOₓ loading from 0.5 to 2.0 mmol, the SA gradually decreased from 1140 to 477 m²/g, and even higher VOₓ of 2.3 mmol drastically decreased SA to 45 m²/g.

3. 2. 2. XRD Analyses

Powder XRD patterns in the 2θ range from 15 to 35° were measured to detect the formation of V₂O₅ crystallites. The XRD patterns of the V(1.0)_PEGₓ catalysts are shown in Fig. 5. No diffraction peaks due to the bulk crystalline V₂O₅ phase were observed in the patterns of V(1.0)-PEGₓ catalysts (Fig. 5 a-c) except for V(1.0)-PEG2 (Fig. 5 a)), which can be attributed either to the absence of V₂O₅ crystallites or to the presence of very small crystallites (< 4 nm), which do not cause distinctive diffraction patterns. The formation of V₂O₅ crystallites was observed in V(1.0)-PEG2. Figure 5 d) and f-i) show the XRD patterns of V-PEG25 with vanadium loading from 1.0 to 2.3 mmol/g. V(1.0)-PEG25 and V(1.5)-PEG25 showed no diffraction peaks for crystalline V₂O₅ (Fig. 5 d) and g)). In contrast, V(2.0)-PEG25 and V(2.3)-PEG25 showed diffraction peaks assignable to V₂O₅ crystallites (Fig. 5 b) and i)).

3. 2. 3. Raman Spectra

Laser Raman spectra were obtained to elucidate the characteristics of vanadium oxide species in the SiO₂ framework. We previously reported the Raman spectra of these materials in Figs. 1 and 2 of ref. 26. The Raman spectra of V(1.0)-PEGₓ samples prepared with different DP of PEGₓ are shown in Fig. 1 of ref. 26. V(1.0)-PEG2 prepared with low-molecular mass PEG (diethylene glycol) showed several distinct peaks at 1040, 996, 925, 704, 483, 405, 306, 289, 197, and 148 cm⁻¹. The Raman band at 1040 cm⁻¹ is assigned to the V = O stretching vibration of isolated monovanadate VO₃⁻32). The bands at 996, 704, 483, 405, 306, 289, 197, and 148 cm⁻¹ correspond to polymeric (V₂O₅)ₓ or crystalline V₂O₅33), and the band at 925 cm⁻¹

is assigned to the perturbed silica vibration, which is indicative of V–O–Si bond formation\textsuperscript{32).} With higher DP of PEG\textsubscript{x} (\textit{x} from 2 to 3), the bands characteristic of crystalline V\textsubscript{2}O\textsubscript{5} showed decreased intensities. Above \textit{x} of 10, the peaks assignable to crystalline V\textsubscript{2}O\textsubscript{5} disappeared, and new peaks appeared at 796, 600, and 488 cm\textsuperscript{-1} that were assigned to SiO\textsubscript{2}\textsuperscript{33).}

The Raman spectra of V\textsubscript{PEG}\textsubscript{25} with different vanadium loadings (0.5 to 2.3 mmol) are shown in Fig. 2 of ref. 26. The band at 1040 cm\textsuperscript{-1} was observed for samples containing 0.5 to 2.0 mmol of VO\textsubscript{x}, and the intensity of this band increased with higher vanadium loading. Above 1.5 mmol of VO\textsubscript{x}, the band ascribed to (V\textsubscript{2}O\textsubscript{5})\textsubscript{x} or crystalline V\textsubscript{2}O\textsubscript{5} appeared at 997 cm\textsuperscript{-1}, and the intensity of this band increased with higher vanadium loading from 1.5 to 2.3 mmol.

3. 2. 4. FT-IR Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy has been used for the characterization of transition metal cation–modified zeolite\textsuperscript{34).} The FT-IR spectra of V(1.0)\textsubscript{PEG\textsubscript{x}} samples prepared with different DP of PEG\textsubscript{x} are shown in Fig. 6. The band at 800 cm\textsuperscript{-1} is ascribed to the symmetric stretching vibration of the Si–O–Si group (SiO\textsubscript{4}\textsuperscript{4–}), and the sharp absorptions observed at 1080 cm\textsuperscript{-1} and 1230 cm\textsuperscript{-1} are assigned to the asymmetric stretching vibrations of Si–O–Si bridges\textsuperscript{35).} The band at 960 cm\textsuperscript{-1} is assigned to a Si–O–metal stretching vibration\textsuperscript{36).}

3. 2. 5. H\textsubscript{2}-TPR

The H\textsubscript{2}-TPR results are shown in Fig. 7. Reduction temperatures in the 450-550 °C range were observed for V–PEG25 samples with VO\textsubscript{x} loadings from 1.0 to 2.0 mmol/g. With higher VO\textsubscript{x} loading, peak areas increased together with a shift to higher reduction temperatures.

3. 2. 6. NMR

Figure 8 shows the $^{29}$Si cross polarization magic angle spinning (CP-MAS) NMR spectra of the as-prepared gel from V(OR), TEOS, and PEG\textsubscript{25}, and its calcined sample (V(1.0)–PEG\textsubscript{25}). The as-prepared gel exhibited resonances at $\sim$ 83, $\sim$ 90, and $\sim$ 98 ppm that are attributable to Si(OEt)\textsubscript{2}(PEG\textsubscript{25})\textsubscript{2}, Si(OEt)(PEG\textsubscript{25})\textsubscript{3}, and Si(PEG\textsubscript{25})\textsubscript{4} with an intensity ratio of 25 : 52 : 23, respectively. This result was consistent with the amount of EtOH generated by the alkoxy-exchange reaction.

The calcined V(1.0)–PEG\textsubscript{25} showed overlapping resonances at $\sim$ 92, $\sim$ 102, and $\sim$ 110 ppm which can be assigned to Si(OSi)\textsubscript{2}(OH)\textsubscript{2}, or Si(OSi)\textsubscript{2}(OV)\textsubscript{2}, framework structures, with \textit{x} values of 2 (Q\textsubscript{2} site), 3 (Q\textsubscript{3} site), and 4 (Q\textsubscript{4} site), respectively. Si(OSi)\textsubscript{2}(OV)\textsubscript{2} and Si(OSi)\textsubscript{3}(OV) are associated with peaks at approximately the same positions as the Q\textsubscript{2} and Q\textsubscript{3} sites\textsuperscript{36).} This NMR spectrum is similar to the $^{29}$Si CP-MAS NMR spectrum of MCM-41, which typically shows broad, overlapping resonances in the $\sim$ 90 to $\sim$ 110 ppm region.
Figure 9 shows the $^{13}$C CP-MAS NMR spectra of PEG25 and the as-prepared gels containing PEG25. PEG25 showed peaks at 60.6, 69.9, and 71.4 ppm, which can be ascribed to $\text{-(OCH}_2\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{OH}$ (1), $\text{-(OCH}_2\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{OSi}$ (2), and $\text{-(OCH}_2\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{OH}$ (3), respectively. The as-prepared gel also showed a new peak appeared at 62.4, which is assigned to $\text{-(OCH}_2\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{OSi}$ (4); in addition, the intensity of the peak at 69.9 ppm increased and a new overlapping peak appeared at 71.9 ppm.

3.3. Catalytic Performance of Isolated VO$_x$ in SiO$_2$ for the Oxidative Dehydrogenation of Ethylbenzene with CO$_2$

We recently reported that V(1.0)$_{\text{PEG25}}$ exhibited very high olefin selectivities and high lattice oxygen conversion of V-site in the ODH of ethane and propane using the lattice oxygen of VO$_3^{2-}$. After the ODH reaction, vanadium species (V$^{5+}$) were reduced to V$^{3+}$ but could easily be reoxidized with air, and constant catalytic performance could be maintained up to ten repeated ODH and regeneration cycles.

CO$_2$ acts as an oxidant for the oxidative dehydrogenation of ethylbenzene (EB) to styrene (ST) with the lattice oxygen of vanadium oxide. Here, we used newly obtained V-PEG$_x$ for the oxidative dehydrogenation of EB using CO$_2$ as a mild oxidant.

Oxidative dehydrogenation of EB was performed at 550 °C under flowing CO$_2$ or Ar over V(1.0)$_{\text{PEGx}}$ (x = 2-50) catalysts as shown in Table 1. With higher DP of PEG$_x$ from 2 to 50, EB conversion increased, and reached a maximum of 60.6 % at DP of 25 with a high ST selectivity of ca. 96 %. In all runs, ST selectivity and yield were higher under CO$_2$ than those under Ar (Runs 1-5).

Runs 4 and 6-9 show the effects of VO$_x$ loading on the oxidative dehydrogenation of EB over V-PEG25 catalysts at 550 °C. In the presence of CO$_2$, with higher VO$_x$ loading from 0.5 to 2.3 mmol, EB conversion and ST yield exhibited volcano type behavior, and ST yield reached the maximum of ca. 58 % at 1.0-2.0 mmol. Even higher VO$_x$ of 2.3 mmol markedly decreased EB conversion to 14.5 %.

4. Discussion

4.1. Gel Formation Process

To investigate the mechanism of gel formation resulting in isolated VO$_3^{2-}$ in the SiO$_2$-framework (matrix), the progress of alcohol-exchange reactions involving two or three components was monitored by analyzing the amounts of alcohols generated during the reaction (Figs. 1 and 2).

Metal alkoxide or carboxylate promotes hydrolytic polycondensation of alkoxysilane compounds. If a small amount of t-BuOH (0.6 mmol) was added to the...
binary system of TEOS (16.7 mmol) and PEG25 (16.7 mmol), the alkoxy-exchange reaction between TEOS and PEG25 formed 21.0 mmol of EtOH at 160 °C, corresponding to 31.5 % of the ethoxy groups of TEOS. These findings indicate that V(OR) or the formed t-BuOH promotes the alkoxy-exchange reaction between TEOS and PEG25.

Together with the findings based on the NMR spectra (Fig. 8), the following should be considered: first, the alkoxy-exchange reactions of OH groups of PEG and TEOS and/or V(OR) proceeded to give a two-dimensional cross-linked macro molecular structure (faster exchange of alkoxy groups up to 2 equivalents of -OH). The subsequent alkoxy-exchange reaction resulted in a gel with a primarily three-dimensional cross-linked structure. Therefore, we propose the following reactions as shown in Scheme 1.

Initially, the alkoxy-exchange reaction between V(OR) (1) and PEG25 proceeded to give (2). The alkoxy-exchange reaction between PEG25 in (2) and TEOS produced (3). Siloxane polycondensation produced (4) by repeated reaction of (2) and TEOS. At this stage, V(OR) and/or t-BuOH catalyzed the condensation of TEOS. Since the molar ratio of TEOS/V(OR) was kept at 16.7 (for a sample containing 1.0 mmol of V), the terminal -OH groups of PEG25 were less likely to react with two V(OR). Vanadium was incorporated in the process of polycondensation of TEOS, as in (7), and two- and three-dimensional cross-linking then formed a simple model structure as in (8) by repeated reactions, as shown in Scheme 1. Silicon atoms at the four corners of (8) were linked with two PEG25. Four inner silicon atoms in (8) were linked with four PEG25, and the other seven silicon atoms were linked with three PEG25. Therefore, the ratio of the three types of different Si atoms linked to PEG is calculated as 26.7 : 46.6 : 26.7. Figure 8 shows that the relative peak intensities of the 29Si CP-MAS NMR
spectra of the as-prepared gel attributed to Si(OEt)(PEG25), Si(OEt)3(PEG25), and Si(PEG25) were 25 : 52 : 23, respectively, although any quantitative discussion requires caution if based on CP-MAS NMR of 29Si1). However, the intensity ratios of these peaks corresponded well to the model structure (8). Unidentified minor resonances in the macro-molecular compounds. Therefore, we limit the discussion requires caution if based on CP-MAS NMR of 29Si1). Therefore, we can attribute the peak at 69.9 ppm to -(OCH2CH2)n-OCH2CH2-OH (1), -(OCH2CH2)n-OCH2CH2-OH (2), and -(OCH2CH2)n-OCH2CH2-OH (3) was 5.0 : 8.4 : 86.6, which disagreed with the relative ratio of carbons of (1), (2), and (3) in PEG calculated as 4 : 4 : 92. This disagreement may originate in the differences in the relaxation times of carbon species in the macro-molecular compounds. Therefore, we limit our qualitative discussion of the 13C CP-MAS NMR spectra results as follows.

The 13C CP-MAS NMR spectra of pure PEG25 in Fig. 9 showed that the intensity of the peak at 69.9 ppm had increased and an overlapping peak at 71.9 ppm appeared as a result of the alkoxy-exchange reaction of TEOS and V(OR) with PEG25. To identify these peaks (69.9 ppm and 71.9 ppm), the amount of PEG25 was doubled in the preparation of gel to give OH/(Or-Bu + OEt) = 2.54 (PEG = 88.6 mmol). The alkoxy-exchange reaction of TEOS and V(OR) with PEG25 then generated 84.8 % of EtOH and 91.4 % of t-BuOH. At this time, the amount of -OSi linked with PEG25 and the free -OH group of PEG25 were calculated as 56.6 mmol (16.7 mmol (TEOS) × 4 (-OEt) × 0.848 (ratio of exchanged EtOH) and 120.6 mmol (88.6 mmol (PEG25) × 2 (-OH) - 56.6 mmol (-OSi linked with PEG25)), respectively, ignoring the quantity of V because V ≪ Si. Similarly, for OH/(Or-Bu + OEt) = 1.27, the amounts of -OSi linked with PEG25 and the free -OH group of PEG25 were 51.0 mmol and 37.6 mmol, respectively. The molar ratios of (free -OH of PEG25)/(-OSi linked with PEG25) were 2.05 (= 120.6/56.6) and 0.74 (= 37.6/51.0) with OH/(Or-Bu + OEt) = 2.54 and 1.27, respectively. If the peak at 69.9 ppm is attributed to -(OCH2CH2)n-OCH2CH2-OH (6), the ratio of the intensity of the peak at 71.4 (3) and 69.9 (2 + 6) ppm should vary in proportion to the molar ratio of free -OH of PEG25/(-OSi linked with PEG25). By deconvolution of the peaks of PEG25, the relative abundances of carbons (1), (2), and (3) were calculated to be 5.0, 8.4, and 86.6 %, respectively. The peak areas of (2 + 6) and (3) are denoted as P2 + 6 and P3, respectively. The ratio areas of P3/P2 + 6 with pure PEG25, V-Si-PEG25-gel (OH/(Or-Bu + OEt) = 2.54), and V-Si-PEG25-gel (OH/(Or-Bu + OEt) = 1.27) were 10.3, 2.6, and 1.3, respectively. These values are consistent with the change in the molar ratio of (free -OH of PEG25)/(-OSi linked with PEG25). Therefore, we can attribute the peak at 69.9 ppm to -(OCH2CH2)n-OCH2CH2-OH (6), and then the overlapping peak at 71.9 ppm can be attributed to -(OCH2CH2)n-OCH2CH2-OH (5).

4.2. Texture of Samples after Calcination

The adsorption isotherms of V-PEGx (Fig. 3(1)) detected no drastic increase in the adsorption of N2 in the mesopore region (p/p0 = 0.3-0.9), indicating that uniform mesopores observed for SBA-15 may not be present in the obtained materials. With higher DP of PEGx, broad pore-size distributions with slight increases in the average pore diameter were observed from the adsorption branches. In V(1.0)-PEGx, wide hysteresis loops closed sharply at a relative pressure of 0.40-0.48. Presumably these hysteresis loops were caused by the pore network effect41). This result strongly suggests that desorption takes place via cavitation of interconnected large pores through narrow necks, which connect the large pores to the outer surface of the particles. Highly ordered three-dimensional close-packed cage-type mesoporous silicas such as SBA-16 and FDU-12 exhibit wide hysteresis loops with sharp adsorption and desorption branches at different relative pressures43,44). Capillary condensation during adsorption is controlled by the cavity size, so the sharp adsorption branch indicates the presence of uniform cavities. In addition, the sharply closing hysteresis loops at specific relative pressure are suggestive of narrow necks in these materials44). Based on these findings, the obtained materials probably contain mesopores with narrow necks and narrow to large random pores corresponding to the DP of PEGx. However, no regular mesopores were observed by transmission electron microscope (TEM) and scanning electron microscope (SEM) (images not shown) in these materials. Therefore, we propose the model of isolated VO43– incorporated in the SiO2 framework as shown in Fig. 10. A similar model was previously proposed with a pore network such as narrow pores connecting the larger pores to the outer surface of the particle41).

Raman spectra (Figs. 1 and 2 in ref. 26) showed bands at 1040 cm–1 and 925 cm–1 ascribed to the V=O stretching vibration in the isolated VO43– species and the V=O-Si bond, respectively, in all samples except for V(2.3)-PEG25. Furthermore, the FT-IR spectra of V(1.0)-PEGx (Fig. 6) showed a band at 960 cm–1 assigned to the Si-O-V vibrations in the vanadium-incorporated SiO2 framework. The finding are generally considered to show incorporation of a heteroatom into the SiO2 framework44). V(1.0)-PEG10-25 with VO43– species incorporated into the SiO2 framework exhibited higher surface areas above 800 m2/g. In contrast, V(1.0)-PEG2 and V(2.0-
PEG25 containing polymeric \((V_2O_5)_n\) and/or \(V_2O_5\) crystallites exhibited lower surface areas below 500 m²/g. These findings indicate that \(V_2O_5\) crystallites were loaded onto the mouths of narrow-neck pores in the isolated \(VO_x\)-incorporated \(SiO_2\)-framework. The XRD patterns detected a small crystalline \(V_2O_5\) phase in V(1.0)\(_{\text{PEG2}}\) and V(2.0)\(_{\text{PEG25}}\) (Fig. 5). In addition, a Raman band at 1040 cm\(^{-1}\) assigned to the \(V\) \(\nu^\prime\) stretching vibration of isolated \(VO_4^{3-}\) species and a band at 996 cm\(^{-1}\) assigned to the \(V\) \(\nu^\prime\) stretching vibration of polymeric \((V_2O_5)_n\) or crystalline \(V_2O_5\) were observed. The peak intensities of isolated \(VO_4^{3-}\) species were higher than those of polymeric \((V_2O_5)_n\) or crystalline \(V_2O_5\) (Figs. 1 and 2 in ref. 26). Therefore, we assumed that these samples contained primarily \(VO_4^{3-}\) species, with minor amounts of polymeric \((V_2O_5)_n\) and crystalline \(V_2O_5\). XRD detected no crystalline \(V_2O_5\) in V(1.0)\(_{\text{PEG3}}\) and V(1.5)\(_{\text{PEG25}}\), but Raman spectroscopy detected major peaks of isolated \(VO_4^{3-}\) species and minor peaks of polymeric \((V_2O_5)_n\) or crystalline \(V_2O_5\), suggesting that isolated \(VO_4^{3-}\) species are the main vanadium species, and polymeric \((V_2O_5)_n\) species are minor species.

H\(_2\)-TPR showed that the reduction peak shifted to a higher temperature region with higher \(V\) content (Fig. 7). Lower reduction temperature seems to be associated with isolated \(VO_4^{3-}\) species, which is consistent with the findings of XRD and Raman spectroscopy. The higher reduction peak observed in V(1.5)\(_{\text{-}}\) and V(2.0)\(_{\text{-}}\)PEG25 is most likely an overlapping peak due to reduction of \(VO_4^{3-}\) in the SiO\(_2\)-framework (480-500 °C) and extra-framework polymeric \((V_2O_5)_n\) (>500 °C). An additional peak was observed at a higher temperature of 570 °C in V(2.3)\(_{\text{-}}\)PEG25, suggesting the co-existence of bulk \(V_2O_5\) at high vanadium loading. A similar trend was reported for VAPO-5 in the reduction of vanadium oxide species\(^{24}\).

The findings of N\(_2\)-adsorption-desorption isotherm, XRD, Raman, FT-IR, and H\(_2\)-TPR indicate that isolated \(VO_4^{3-}\) was dispersed in the SiO\(_2\)-framework for catalysts prepared with moderate \(x\) (from 10 to 50) and lower vanadium loadings (below 1.0 mmol). In contrast, isolated \(VO_4^{3-}\) species were incorporated into the SiO\(_2\)-framework and \(VO_x\) species such as polymeric \((V_2O_5)_n\) and/or crystalline \(V_2O_5\) were formed outside the framework for PEG\(_x\) of lower \(x\) (\(x\) of 2 and 3) and higher vanadium loadings (above 1.5 mmol).

In order to explain the mechanism of formation of crystalline \(V_2O_5\), the amounts of formed alcohols were determined for V(1.0)\(_{\text{-}}\)PEG2. The reactivity of PEG2 in the alkoxy-exchange reaction was much higher than that of PEG25, as the amounts of recovered EtOH and t-BuOH were larger at a lower temperature of 50 °C as compared to the reaction with PEG25. The alkoxy-exchange reaction of TEOS and \(V(OR)\) with PEG2 formed 1.4 % and 8.0 % of EtOH and t-BuOH, respectively, even at 50°C, indicating that the reaction of \(V(OR)\) and PEG2 proceeded preferentially. Therefore, the reaction forming V-O-PEG-O-V (hereafter V-O-L\(_{-}\)O-V, L: PEG unit) could not be eliminated in the initial stage, and these products resulted in the formation of polymeric \((V_2O_5)_n\) after calcination. Consequently, there must be similar alkoxy-exchange rates between \(V(OR)\) and TEOS with PEG to obtain isolated \(VO_4^{3-}\) species in the SiO\(_2\) framework.

To clarify the contribution of cross-linked Si-O-L-O-Si in the gel to the high surface area, diethylene glycol mono-ethyl ether (PEG2EE) and polyethylene glycol...
mono-methyl ether (PEGME; \(x = 17-18\)) were used instead of PEG\(x\). The alkoxy-exchange reactions of TEOS and V(OR) with PEG2EE or PEGME proceeded to 93.9 % and 86.9 % completion for PEG2EE, and 91.4 % and 93.2 % completion for PEGME, respectively, with an OH/(Or-Bu+ OEt) ratio of 1.27. Therefore, almost all ethoxy and butoxy groups of Si and V were exchanged to form Si(PEG2EE)\(_4\) and V(PEG2EE)\(_3\)O or Si(PEGME)\(_4\) and V(PEGME)\(_3\)O. Calcination of the obtained viscous solution (no gel was obtained due to the absence of cross-linking) at 600 °C in air to eliminate PEG2EE formed V-PEG2EE containing V\(_2\)O\(_5\) crystallites detected by XRD and Raman (Fig. 11 a) and Fig. 12 a)) with low SA of 331 m\(^2\)/g and TPV = 0.20 mL/g. In contrast, V-PEGME was formed containing isolated VO\(_4^{3-}\) species detected by Raman spectroscopy (Fig. 11 b) and Fig. 12 b)) with high SA of 931 m\(^2\)/g and TPV = 0.89 mL/g. Based on these findings, we propose the following conditions for the formation of isolated VO\(_4^{3-}\) species: i) Before calcination of the alkoxy-exchanged precursor, vanadium species must be separated at certain distances; ii) Chemical cross-linking by a larger molecular weight PEG can satisfy the above conditions, but such conditions are not fulfilled with low molecular weight diols; iii) No chemical cross-linking is possible with PEGME (\(x = 17\)), but long PEGME chains of vanadium species may generate entanglement of polymer chains between large excess Si(PEGME)s, and such polymer chain entanglements could be considered to represent physical cross-linking.

To understand the effect of differences in DP of PEG\(x\) during calcination, differential thermogravimetric analysis was carried out on gels or viscous solutions of V(1.0)-PEG\(x\), as compared in Fig. 13.

In the case of V(1.0)-PEG2, a very sharp weight decrease due to combustion and/or decomposition of the PEG2 moiety in the gel was observed at a temperature range of 280-290 °C, indicating that the gel was very homogeneous. In contrast, combustion and/or decomposition peaks for DP larger than 10 were broad, probably due to the non-uniform gel structures. The total weight losses in these samples increased in the following order: V(1.0)-PEG2EE, V(1.0)-PEG2, V(1.0)-PEG10, V(1.0)-PEG25, and V(1.0)-PEGME, corresponding to 88.3, 89.5, 92.0, 94.3, and 98.4 %, respectively. This order depended on the mass of PEG incorporated into the samples as expected for V(1.0)-PEG2EE and V(1.0)-PEG2. Moreover, weight loss occurred at temperatures as low as 180 °C due to degradation of the PEG polymer chain. With higher DP of PEG\(x\), the broad combustion peak of reacted or free PEG\(x\) (or PEG2EE, PEGME) shifted to the higher temperature side. With higher DP of PEG\(x\), the mass of PEG per unit mass of gel increased, and highly cross-linked gels such as (8) (Scheme 1) hindered decomposition of the PEG moiety. Hence, decomposition and/or combustion of the PEG moiety in the gel proceeded slowly, which prevented aggregation of VO\(_4^{3-}\) species in the Si-O-Si matrix, leaving isolated VO\(_4^{3-}\) species in the SiO\(_2\)-framework. Cross-linking such as Si-O-L-O-Si is not necessary to give isolated VO\(_2\) species in the SiO\(_2\)-
framework, since the use of PEG monomethyl ether afforded a similar material (Fig. 11 b), Fig. 12 b), and Fig. 13 d).

Monotonous increases in pore volumes with higher DP of PEGx seem to be associated with the mass of PEG incorporated into the gel. In contrast, small increases in average pore diameters with higher DP of PEGx seem to increase the Si–O–L–O–Si distances in the cross-linked gel.

Comparison of the peaks of V(1.0)-PEG2 and V(1.0)-PEG2EE in Fig. 13 showed the presence of a major amount of V─O─L─O─Si linking in the V(1.0)-PEG2 gel resulted in formation of a small amount of crystalline V2O5 during calcination, whereas the absence of V─O─L─O─Si or V─O─L─O─V linking in V(1.0)-PEG2EE solution led to crystalline V2O5. Therefore, the formation of crystalline V2O5 in V(1.0)-PEG2 was somewhat inhibited by the presence of Si–O─L─O─V─O─L─O─Si linking.

The above results suggest that linking of Si–O─L─O─Si may not be necessary if PEGx with higher DP (10-50) is used. Since PEG chains including terminal methoxy groups of Si(PEGME)x and V(PEGME)xO may be closely entangled with each other, use of V(1.0)-PEG10-50 and V(1.0)-PEGME resulted in the same physical characteristics after calcinations.

4.3. Oxidative Dehydrogenation of EB

Use of CO2 as a mild oxidant has been proposed for the oxidative dehydrogenation of EB27,29,38). Here, the possibility of redox behavior between CO2 and isolated vanadium species in the SiO2 framework was examined.

The results of the oxidative dehydrogenation of EB in CO2 and Ar (runs 4 and 9 in Table 1), and Raman spectroscopy (Figs. 1 and 2 in ref. 26) showed that the oxidative dehydrogenation of EB proceeded mainly on the isolated VOx3 species (V(1.0)-PEG25) and ODH scarcely proceeded on the crystalline V2O5(V(2.3)-PEG25). The oxidative dehydrogenation of EB to ST occurred at the redox site of the isolated vanadium species29,38). The active lattice oxygen of isolated VOx3 species activated the EB molecule through abstraction of the α-hydrogen, which formed reduced isolated VOx3 and released H2O. The reduced isolated VOx3 species was re-oxidized to the original oxidation state (V5+) by CO2.

After the ODH of EB over V(1.0)-PEG25 under CO2 and Ar, the samples were characterized with Raman spectroscopy (spectra are not shown). After reaction under Ar, the peak at 1040 cm⁻¹(V = O (VOx3)) disappeared. In contrast, after reaction under CO2, the catalyst maintained a weak peak at 1040 cm⁻¹. These findings indicate that CO2 could re-oxidize VOx3 to VOx3 to maintain the catalyst activity for ODH.

5. Conclusions

VOx species incorporated into the SiO2-framework were first synthesized via alkoxy-exchange reactions with Si(OEt)x, V(O–Bu)yO, and PEG. The alkoxy-exchange reaction of Si(OEt)x and PEG was promoted by V(O–Bu)yO or t-BuOH formed from V(O–Bu)yO. Based on the findings of 29Si CP-MAS NMR and the amounts of alcohols generated by the alkoxy-exchange reaction, the structure of the obtained gel was considered to consist of three-dimensionally cross-linked materials excluding Si(OEt)x(PEG).

Similar alkoxy-exchange rates between alkoxides of vanadium and silicon with PEG were important to obtain isolated VOx species in the SiO2-framework after calcination at 600 °C in air to eliminate PEGx. Vanadium species in the catalysts differed by the DP of PEG and the vanadium content. Isolated VOx3 was dispersed in the SiO2 framework of catalysts prepared with a higher DP of PEG (over 10) and lower vanadium content (below 1.0 mmol). In addition, the alkoxy-exchanged precursor had chemical cross-linking (use of PEG) or the physical cross-linking (use of PEGME).

In both case, the isolated VOx3 species were generated, and the vanadium species must be separated at certain distances before calcination of the alkoxy-exchanged precursor.

V(1.0)-PEGx with very high surface area of ~1000 m²/g, narrow neck pore entrances, and randomized inside mesopores was obtained.

The oxidative dehydrogenation of ethylbenzene under CO2 proceeded on the isolated VOx3 species in the SiO2 framework with a high ethylbenzene conversion and high selectivity for styrene, and the reduced isolated VOx3 species during dehydrogenation could be re-oxidized to the original oxidation state (V5+) with CO2.

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要旨
金属アルコキシドとポリエチレングリコールのアルコキシ交換反応による
孤立VO₂⁺種含有シリカの調製

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新規 VO₃⁻SiO₂触媒調製におけるアルコキシ交換反応による
ゲルの生成過程および孤立したバナジウムの生成メカニズムについて詳細な検討を行った．焼成前後のサンプルの窒素吸着,
XRD, Raman, FT-IR, H₂-TPR, NMR などによるキャラクタリゼーションの結果，バナジウムが孤立した状態で大きな
比表面積を持つシリカ骨格に取り込まれるためには，バナジウムプトキジドのアルコキシ交換速度とテトラエトキシシランの
アルコキシ交換・縮合速度が同等でなければならないこと，この
ためには過剰の分子量のPEGの使用が不可欠であることを
明らかにした．また，新規 VO₃⁻SiO₂触媒の高い酸化還元特性
に着目し，温和な酸化剤であるCO₂を用いたエチルベンゼン
の酸化脱水素反応を検討した．その結果，CO₂存在下において,
高いエチルベンゼン転化率およびスチレン選択率を示した．