

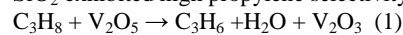
# Oxidative dehydrogenation of alkanes over vanadium oxide prepared with V(*t*-BuO)<sub>3</sub>O and Si(OEt)<sub>4</sub> in the presence of polyethyleneglycol

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## Introduction

Vanadium-based catalysts have been used for oxidative dehydrogenation (ODH) of alkanes [1]. In particular, V-incorporated into mesoporous silica frame such as V-MCM-41 and V-MCM-48 have been reported to exhibit high activity for ODH of propane (ODHP) [2].

The objective of this work is to obtain higher concentration of vanadium oxide species incorporated into SiO<sub>4</sub><sup>4-</sup>-based frame using polyethyleneglycol (PEG), vanadium alkoxide and TEOS. To achieve this, the sol-gel method was employed. We have found that thus obtained V-SiO<sub>2</sub> exhibited high propylene selectivity for the ODHP with lattice oxygen (reaction 1).



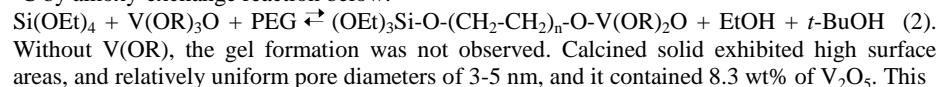
## Experimental

A high surface area V-SiO<sub>2</sub> was synthesized from TEOS and V(*t*-BuO)<sub>3</sub>O (V(OR)) under N<sub>2</sub> atmosphere in the presence of PEG (ethylene oxide unit *x* = 3, 10 and 25). Above mixed solution (toluene as solvent) was heated from 50 to 130 °C for 5 h and then at 140 °C for 1 h under reduced pressure. After pulverizing the residual gel, it was calcined at 600 °C for 5 h in air. The obtained materials were denoted as V-SiO<sub>2</sub>-PEG<sub>x</sub>. For comparison, V/SiO<sub>2</sub> was prepared by impregnating an aqueous solution of NH<sub>4</sub>VO<sub>3</sub> with SiO<sub>2</sub> (SA = 283 m<sup>2</sup>/g) and the catalyst precursor was calcined at 600 °C for 5 h in air.

The ODH reaction was carried out with a fixed-bed flow-type quartz reactor equipped with two feed systems of propane and air at 450 °C. Before the reaction, the catalyst was treated with air at 450 °C for 30 min. Reaction products were analyzed with an on-line gas chromatograph (hydrocarbons and H<sub>2</sub>) and an FID gas chromatograph (CO, CO<sub>2</sub>) equipped with a methanizer.

## Results/Discussion

Reaction of TEOS and V(OR) in the presence of PEG<sub>x</sub> afforded a gel during heating at 50-130 °C by alkoxy-exchange reaction below:



value is ten times larger than that in V-MCM-41 [2].

Figure 1 shows Raman spectra of V/SiO<sub>2</sub> and V-SiO<sub>2</sub>-PEG<sub>x</sub>. V/SiO<sub>2</sub> (Fig. 1a) exhibited a weak broad peak at 1040 cm<sup>-1</sup> and sharp peaks at 996, 704, 526, 487, 405, 289, 205 and 147 cm<sup>-1</sup>. The peak at 1040 cm<sup>-1</sup> is assigned to the V=O vibration of isolated tetrahedral monovanadate VO<sub>4</sub><sup>3-</sup>, and the peaks at 996, 704, 526, 487, 405, 289, 205 and 147 cm<sup>-1</sup> correspond to V<sub>2</sub>O<sub>5</sub> crystallites. On the other hand, V-SiO<sub>2</sub>-PEG<sub>x</sub> exhibited a sharp peak at 1040 and broad peaks at 920, 800 and 496 cm<sup>-1</sup> except for V-SiO<sub>2</sub>-PEG<sub>3</sub>. V-SiO<sub>2</sub>-PEG<sub>3</sub> exhibited additional weak broad peaks 996, 704, 289 and 147 cm<sup>-1</sup>. With an

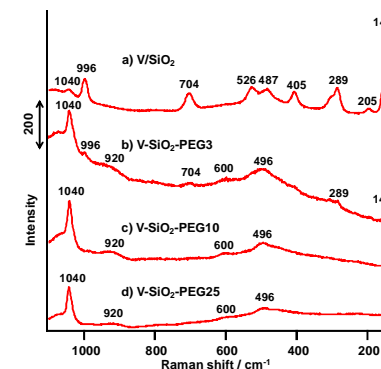


Figure 1 Raman spectra of V/SiO<sub>2</sub> and V-SiO<sub>2</sub>-PEG<sub>x</sub> catalysts

increase in the molecular weight (Mw) of PEG (ethylene oxide unit from 3 to 25), the amount of isolated VO<sub>4</sub><sup>3-</sup> species increased.

Table 1 summarizes the results of the ODHP over V/SiO<sub>2</sub> and V-SiO<sub>2</sub>-PEG<sub>x</sub> using lattice oxygen of vanadium oxide. V/SiO<sub>2</sub> (Run 1) afforded propylene selectivity of 81.5% with propane conversion of 2.2%. The ratio of propane fed to the catalyst and lattice oxygen in the V/SiO<sub>2</sub> (200 mg) was 3.8. When V<sub>2</sub>O<sub>5</sub> was reduced to V<sub>2</sub>O<sub>3</sub> by reaction (1), the maximum conversion of propane is estimated to 11.3%. Therefore, propane conversion of 2.2% corresponds to 19.5% of the theoretical conversion.

As seen in runs 2 to 4, with an increase in the Mw of PEG, propane conversion slightly increased from 1.6 to 2.0%. It must be noted that a very high propylene selectivity of 95% could be achieved with these catalysts. These results indicate that propylene selectivity is closely related to the amount of isolated VO<sub>4</sub><sup>3-</sup>. After ODH reaction, the used catalyst was completely re-oxidized to the original form according to reaction (3).

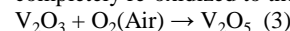


Table 1 Effect of preparation method on ODHP

Run	Catalyst	Catalyst SA [m <sup>2</sup> /g]	C <sub>3</sub> H <sub>8</sub> Conv [%]	Selectivity[%]				Yield[μmol]		C <sub>3</sub> H <sub>6</sub> yield[%]	C <sub>3</sub> H <sub>6</sub> <sup>a)</sup> yield[%]
				C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	Carbon	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>		
1	V/SiO <sub>2</sub>	228	2.2	81.5	10.4	5.7	2.3	29.5	0.3	1.8	15.9
2	V-SiO <sub>2</sub> -PEG3	700	1.6	94.5	0.5	1.8	3.0	25.4	0.2	1.6	14.2
3	V-SiO <sub>2</sub> -PEG10	830	1.9	95.3	0.1	0.7	3.6	29.5	0.3	1.8	15.9
4	V-SiO <sub>2</sub> -PEG25	978	2.0	94.6	0.8	1.4	3.0	31.5	0.2	1.9	16.8

Catalyst: 200 mg, Metal oxide: 1.0 mmol/g-SiO<sub>2</sub>, SiO<sub>2</sub> surface area: 283 m<sup>2</sup>/g, pretreatment: O<sub>2</sub>/Ar = 5/20 (mL/mL/min), 30 min at 450 °C

Flow rate: C<sub>3</sub>H<sub>8</sub>/Ar = 5/20 (mL/mL/min), reaction time: 8 min, reaction temperature: 450 °C

<sup>a)</sup> Yield based on lattice oxygen

## References

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2. M. L. Pena, A. Dejoz, V. Fornes, F. Rey, M. I. Vazquez, J.M. Lopez Nieto, Appl. Catal. A **209**, 155 (2001)