EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Carbon Dioxide as Feedstock in Selective Oxidation of Propane

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201701049

Link to VoR: http://dx.doi.org/10.1002/ejic.201701049

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FULL PAPER

Carbon Dioxide as Feedstock in Selective Oxidation of Propane

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Abstract: Carbon dioxide is a promising nonconventional oxidant for catalytic dehydrogenation of lower alkanes to olefins. Lower catalytic activity of CO_2 as compared to oxygen that is typically used in oxidative dehydrogenation (ODH) also means that more reactive olefins are less likely to undergo undesirable combustion in the presence of CO_2. Supported vanadia catalysts synthesized by incipient wetness impregnation of silica support, and by varying the surface coverage of VO_x species using sodium on the silica surface, the nature of the catalyst was investigated. The promotion with Na cations significantly improved the dispersion of surface VO_x species and resulted in the formation of surface Na-metavanadate or another reduced V^{3+}/V^{4+} phase, which lacked catalytic activity in propane ODH in the presence of CO_2.

Introduction

Carbon dioxide (CO_2) and C2-C3 alkanes are well-known greenhouse gases that are generated by human. Our planet is projected to undergo significant environmental changes this century with potentially devastating consequences for the global economy and the natural world if humanity fails to reduce CO_2 emissions from burning fossil fuels. The electricity and heat generation combined with the use of hydrocarbon-based fuels in transportation have been the largest contributors of CO_2, creating almost two-thirds of global emissions (e.g., 5,271 million metric tons of the total U.S. energy-related CO_2 emissions in 2015).[1] On the other hand, natural gas production continues to increase as shale gas is rapidly becoming an alternative source of natural gas and its production is currently one of the fastest growing segments of the US oil and gas industry.[2] While C2-C3 alkanes are the major components of shale gas, they currently have no significant applications as chemical feedstocks due to high chemical stability of these molecules and the lack of technologies that can transform them selectively into chemical intermediates. Therefore, it is highly desirable to develop novel chemical processes that can jointly employ CO_2 and C2-C3 alkanes in chemical synthesis.[1, 3] The total annual amount of CO_2 used in industry as a chemical feedstock to make urea, inorganic carbonates, pigments, methanol and salicylic acid, is approximately two orders of magnitude lower than its annual atmospheric emissions.[4] Therefore, it is highly desirable to develop new large-scale chemical processes that utilize CO_2 to more fully explore the potential of its fixation into value-added products.

Selective oxidation of lower alkanes has been a long-standing fundamental and practical challenge, primarily due to inertness of C-H bonds (e.g., the secondary C-H bond energy of 96 kcal/mol in propane) requiring energy-intensive conditions to achieve practical conversion and limited process selectivity due to greater reactivity of the partial oxidation products, e.g., propylene.[5,6] Recent reports indicated that CO_2 is a mild oxidant that can perform oxidative dehydrogenation (ODH) of lower alkanes (C2-C4) into corresponding olefins (1), all of which are highly valuable chemical intermediates:

$$C_nH_{2n+2} + CO_2 \rightarrow C_nH_{2n} + CO + H_2O \qquad (1)$$

Ethane and propane ODH by CO_2 is expected to produce a 1:1 molar mixture of olefins with carbon monoxide that can be directly used in a variety of downstream chemical processes, such as co-polymerization to produce valuable thermoplastic poly-ketones[7] and hydro-formylation[8] to make a variety of aldehyde intermediates.

Supported vanadia and chromia catalysts have been identified in recent studies as the most promising catalysts for lower alkane ODH by CO_2.[9-15] These catalysts are typically synthesized by incipient wetness impregnation of oxide supports, such as SiO_2, Al_2O_3, CeO_2, and ZrO_2, by solutions of V(V) and Cr(III) precursors, such as ammonium metavanadate (NH_4VO_3) and Cr(III) nitrate, followed by drying and thermal activation at ~350°C in air to produce well-dispersed, tetrahedrally coordinated molecular VO_x and CrO_x species on the surface of oxide supports. The catalytic activity and selectivity of these supported VO_x and CrO_x catalysts in lower alkane ODH is associated with the presence of monomeric and polymeric VO_x and CrO_x species at sub-monolayer surface coverage. Therefore, the catalytic behavior of these catalysts may be tuned by varying the surface coverage of VO_x and CrO_x species, the nature of the oxide support, and addition of promoter species.[9-15]

In a recent study,[15] the silica-supported vanadia catalysts have been extensively investigated and found to be highly promising for the propane ODH using molecular oxygen. However, the silica-supported catalysts display significantly lower monolayer coverage of vanadia (ca. 3.3 V/nm^2) as compared to other, more reactive oxide supports, such as alumina (7-9 V/nm^2). The promotion of silica with Na^+ cations resulted in significantly enhanced dispersion of monomeric vanadia species on SiO_2.[16] This effect was found to be optimal at a Na^+/V ratio of 0.2, and above this ratio the formation of sodium metavanadate resulted in the loss of catalytic activity. According to Grant et al.,[16] the Na^+ reacts with surface silanols to form more reactive $Si-O-Na^+$ anchoring sites that bond to several monomeric vanadia species. Therefore, the use of the Na^+ species to promote VO_x dispersion on the silica surface offers new opportunities to design novel 2D metal oxide catalysts supported on SiO_2. According to Grant et al.,[16] greater surface coverage of 2D vanadia species in Na-promoted catalysts leads to higher propane ODH rate while maintaining high propylene selectivity. However, the behavior of Na-promoted vanadia catalysts in propane ODH by CO_2 has not

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10.1002/ejic.201701049

been investigated. Therefore, in this study we synthesized Na-promoted vanadia catalysts supported on silica and investigated their behavior in two propane ODH reactions employing molecular oxygen and CO_2.

Results and Discussion

Table 1 shows the composition of model supported vanadia catalysts synthesized in this study. A series of VO_x/SiO_2 catalysts were synthesized at different vanadia loadings to study the effect of vanadia surface coverage on conversion and selectivity in propane ODH. The vanadia surface coverage[16] in these catalysts ranged from 54 to 185% of a theoretical monolayer on the silica support in the absence of Na^+, and from 21 to 72% for the Na-promoted silica.

Table 1. Vanadium content in silica-supported catalysts.

Samples	V %*	V/nm^2	Coverage, % monolayer	
			Silica	Na promoted
S1 or Na-S1	4.2	1.9	54.0	21.2
S2 or Na-S2	6.9	3.1	88.0	34.4
S3 or Na-S3	9.1	4.1	117.1	45.6
S4 or Na-S4	14.7	6.6	185.7	72.2

[a] * The vanadium content (wt. %) was analysed by EDS.

The occurrence of homogeneous reactions was investigated first by passing the above-mentioned propane/O_2 and propane/CO_2 mixtures through an empty reactor and over the original silica support at 550-750°C. For an empty reactor, trace amounts of ethylene and methane were detected above 650°C for the propane/O_2 mixture, while no reaction was observed for the propane/CO_2 mixture at any temperature. Similar results were observed for the ODH reactions over the original silica support, i.e., trace levels of ethylene and methane above 550°C for the propane/O_2 mixture. Moreover, no reaction products were observed up to 700°C for the propane/CO_2 mixture, while above 700°C, CO and a trace amount of propane cracking products were observed. However, we observed the occurrence of homogeneous combustion reaction over silica support in the presence of O_2 above 600°C, as well as cracking reaction products when the reactor temperature was further increased to 700°C. However, no reactions were observed over the silica support at relevant temperatures (600°C and below) employed in this study to investigate propane ODH reactions. Moreover, while propane ODH in the presence of O_2 and CO_2 was investigated over silica-supported vanadia catalysts at 350-600°C, significant propane conversion was observed only at 550 and 600°C.

Table 2. Propane ODH reactions over VO_x/SiO_2 catalysts at 550°C.

V/nm^2	Oxidant	C_3H_8 conv. (%)	Coverage, % monolayer					Yield (%)
			CO	CO_2	CH_4	C_2H_4	C_3H_6	
1.9 (S1)	O_2	18.7	28.1	15.6	16.4	0.0	39.3	
	CO_2	9.2	60.6	-	0.0	0.0	39.4	7.4
3.1 (S2)	O_2	27.3	26.4	0.0	32.0	0.0	41.6	3.6
	CO_2	25.0	51.5	-	3.4	0.0	45.1	11.4
4.1 (S3)	O_2	37.2	28.0	13.6	49.0	1.0	9.4	11.3
	CO_2	29.4	86.8	-	3.4	0.0	9.8	3.5
6.6 (S4)	O_2	38.5	18.0	8.5	40.0	5.3	28.0	2.9
	CO_2	22.3	77.6	-	0.0	0.0	22.4	10.8

Reaction conditions; 550°C, GHSV = 2500 h^{-1}, O_2 : C_3H_8 = 1:2, CO_2 : C_3H_8 = 2:1, He balance

Table 2 shows the initial propane conversion and product selectivity of propane ODH over VO_x/SiO_2 catalysts at 550°C. In the case of O_2, the formation of C1 and C2 products increased with vanadia content in these catalysts. Also, as expected the conversion of propane was considerably higher during O_2 ODH as compared to CO_2 ODH reaction. However, the propylene yield was similar for both CO_2 and O_2 ODH reactions due to a greater extent of cracking reactions during O_2 ODH. Also, the propane conversion over S1 catalyst (1.9 V/nm^2) was 18 mol.% for O_2 ODH and 9.2 mol. % for CO_2 ODH, while it increased with vanadia content, e.g., to 25 mol. % for the S2 catalyst for both O_2 and CO_2 ODH reactions, until reaching a maximum for the S3 catalyst. The maximum yield of propylene of ca. 11 mol. % was observed over S2 catalyst (3.1 V/nm^2). It should be noted that the S1 catalyst corresponded to ca. 50% of theoretical monolayer coverage of vanadia on silica, whereas the S2 and S3 catalysts are characterized by ca. 90% monolayer and 120% monolayer coverages, respectively. Therefore, based on initial reactivity of VO_x/SiO_2 catalysts in these 2 ODH reactions, one may conclude that the presence of a monolayer of surface VO_x species is important for the reactivity in these propane ODH reactions.

Table 3. Propane ODH reactions over VO_x/SiO_2 catalysts at 600°C.

V/nm^2	Oxidant	C_3H_8 conv. (%)	Coverage, % monolayer					Yield (%)
			CO	CO_2	CH_4	C_2H_4	C_3H_6	
1.9 (S1)	O_2	22.9	27.7	14.6	15.5	9.5	32.9	7.5
	CO_2	13.7	50.9	-	9.0	0.0	40.2	5.5
3.1 (S2)	O_2	33.4	6.8	18.8	25.0	18.9	30.4	10.1
	CO_2	29.2	69.0	-	9.7	0.0	21.4	6.3
4.1 (S3)	O_2	52.1	28.0	10.3	47.0	4.8	10.3	5.4
	CO_2	50.7	84.7	-	4.0	0.0	11.3	5.7
6.6 (S4)	O_2	45.9	23.8	14.9	39.0	7.0	15.0	6.9
	CO_2	31.1	71.7	-	13.2	2.5	12.6	3.9

Reaction conditions; 600°C, GHSV = 2500 h^{-1}, O_2 : C_3H_8 = 1:2, CO_2 : C_3H_8 = 2:1, He balance

Table 3 shows the initial propane conversion and product selectivity results for propane ODH over VO_x/SiO_2 catalysts at 600°C. The propane conversion and formation of C1-C3 cracking products increased dramatically at 600°C, while the propylene yield was not significantly affected. The main difference in reaction products observed for CO_2 and O_2 ODH reactions was significant amount of CO produced in the former case and methane for O_2 ODH. C2 product (ethane and ethylene) was not observed among the reaction products during CO_2 ODH, except over the S4 catalyst (6.6 V/nm^2) at 600°C that contained ca. 180% theoretical monolayers of VO_x species. However, ethylene and CO_2 were already observed low temperature (450°C) during O_2 ODH. The conversion of propane increased with VO_x coverage reaching a maximum over the S3 catalyst and then declining at higher VO_x coverage.

Turnover Frequencies (TOF) for propane consumption were calculated by eq. (2):

$$TOF = \frac{\dot{n}_{C_3H_8,0} \cdot X_{C_3H_8} \cdot M_V}{m_{cat} \cdot w_v \cdot 10^{-2}} \qquad (2)$$

TOFs report the numbers of propane molecules converted at each VO_x species per second, where $\dot{n}$ denotes the molar flowrate of propane (mol/s), X the fractional conversion, M_v the molar mass of vanadium (g/mol), m_{cat} the catalyst weight (g) and W_V the vanadium content by mass (wt. %). Figure 1 shows the TOFs for propane consumption as a function of surface VO_x coverage at 500°C under different space velocity to maintain low propane conversion (<15%). All supported vanadia catalysts displayed very similar TOF values except for the S1 catalyst (at the lowest V content). Also for the S2 and 3 catalyst (3.1 and 4.1 V/nm^2 close to theoretical monolayer coverage) it showed the maximum TOF value was observed but the values only varying from 3.8 to 4.1 × $10^{-3}s^{-1}$ among three vanadia catalysts of S2, S3 and S4.

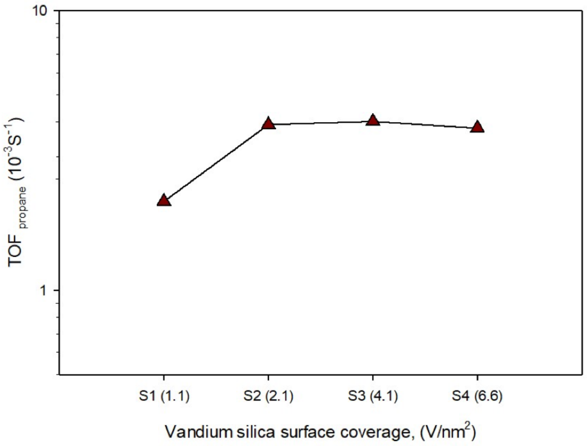

Figure 1. Propane consumption TOFs as a function of surface VO_x coverage at 500°C determined at propane conversion of ~15%.

All supported vanadia catalysts were further investigated at 550 and 600°C, GHSV=2500 h^{-1}, and feed composition of CO_2:C_3H_8 = 2:1 (Figures S1-S4) as a function of time on stream. The S1 catalyst (1.9 V/nm^2) initially displayed low catalytic activity at 550°C, which was subsequently lost after 2 h under catalytic reaction conditions, while stable catalytic behavior was observed at 600°C for more than 3.5 h. The S2 catalyst (3.1 V/nm^2) initially showed high catalytic activity, which continuously declined with time at 550°C. The formation of C1 and C2 products dramatically increased at 600°C after 3 h on stream, while propane conversion and propylene selectivity decreased. On the other hand, the catalytic activity rapidly decreased over the S3 catalyst (4.1 V/nm^2) with time on stream. These results indicated that the VO_x/SiO_2 catalysts rapidly deactivate with increasing VO_x content above the theoretical monolayer coverage. The catalytic activity did not increase with reaction temperature, while the selectivity to propylene decreased at the expense of propane cracking reactions. Moreover, the S2 and S3 catalysts which showed a higher conversion for CO_2 ODH of propane tended to deactivate rather quickly with time on stream. Also deactivation of the S2 and S3 catalysts was accelerated at higher reaction temperature of 600°C, as propane conversion decreased by ca. 50% after 1 h under catalytic reaction conditions. These results suggested that more limited extent of surface reoxidation with increased VO_x coverage may be responsible for the decreased ODH activity of VO_x/SiO_2 catalysts.

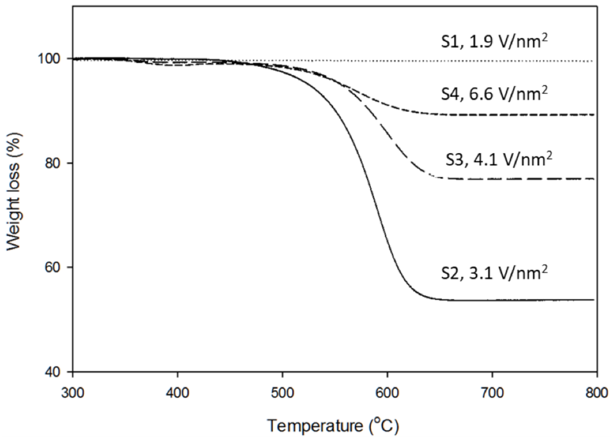

Figure 2. TGA curves in air for VO_x/SiO_2 catalysts after CO_2 ODH of propane at 600°C for 72 h.

Figure 2 shows the TGA curves for used VO_x/SiO_2 catalysts after CO_2 ODH of propane at 600°C for 72 h. All used catalysts exhibited a weight losses during TGA in air associated with carbon deposition, whereas used catalysts after O_2 ODH showed very little weight loss features in TGA. In a recent paper, Ascoop et al.,[17] also reported significant carbon deposition even after a short time on stream during CO_2 ODH of propane over VO_x/SiO_2 catalysts. The extent of carbon deposition varied with varying vanadium content, with two catalysts at near monolayer coverage, i.e., S2 (3.1 V/nm^2) and S3 (4.1 V/nm^2) showing much higher weight loss, ca. 45 and 20 wt. %, respectively, while the S1 (1.9 V/nm^2, ca. 0.5 monolayer) showed almost no weight loss during TGA measurement. These observed differences in carbon deposition behavior may be related to catalytic activity, since the

Table 4. CO_2 ODH of propane reaction results over sodium-promoted silica catalyst with various vanadium content.

Samples	Temp. (°C)	C_3H_8 conv. (%)	Selectivity (%)			
			CO	CH_4	C_2H_4	C_3H_6
1.9	550	1.3	100	0.0	0.0	0.0
(Na-S1)	600	3.4	6.3	8.2	85.5	0.0
3.1	550	0.9	100	0.0	0.00	0.0
(Na-S2)	600	2.2	5.5	8.3	86.2	0.0
4.1	550	0.9	100	0.0	0.00	0.0
(Na-S3)	600	4.3	6.3	8.3	85. 5	0.0
6.6	550	1.8	100	0.0	0.0	0.0
(Na-S4)	600	5.5	4.0	8.0	88.0	0.0

Reaction conditions; GHSV = 2500 h^{-1}, O_2 : C_3H_8 = 1:2, CO_2 : C_3H_8 = 2:1, He balance

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catalysts showing higher reactivity in CO_2 ODH of propane displayed greater carbon deposition. These results suggested that the acidic silica support may also play a role in initiating carbon deposition by adsorbing hydrocarbon intermediates during the ODH reaction in the presence of CO_2. However, the exposure of the silica surface to hydrocarbon intermediates is minimized above the monolayer coverage of the VO_x species, e.g., for S4 (6.6 V/nm^2), explaining diminished carbon deposition observed for this catalyst (ca. 2% weight loss).

Na-promoted silica support were employed to improve surface dispersion of two-dimensional VO_x species. Table 4 shows CO_2 ODH of propane reaction results over Na-promoted VO_x/SiO_2 catalysts prepared at the same VO_x surface coverage as the Na-free supported VO_x catalysts (Table 1). Unlike Na-free catalysts, Na-promoted VO_x/SiO_2 catalysts showed no selectivity to propylene instead displaying increasing tendency to form cracking products, ethane and methane, with increasing vanadium content. The Na-promoted catalysts showed very low catalytic activity at 550 and 600°C. A high reaction temperature of 600°C, a selectivity more than 85% to ethylene was observed over all the catalysts while at the reaction temperature of 550°C only CO was observed with very low propane conversion of less than 2%. The selectivity to C2 species (ethane and ethylene) was particularly high and remained relatively constant over all catalysts investigated, suggesting that these species may represent reaction intermediates during propane/propylene degradation to methane.

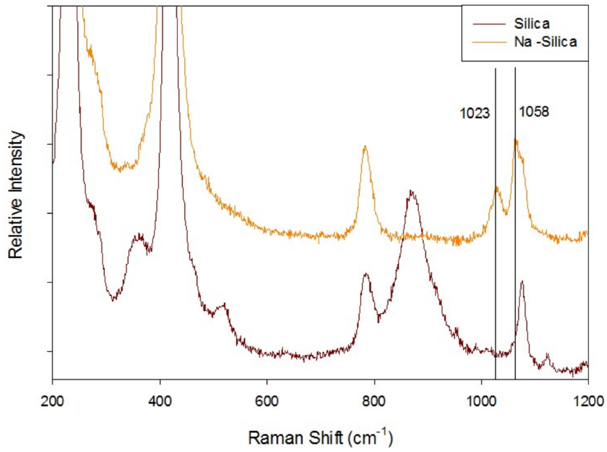

Figure 3. Raman spectra of the original and Na-promoted silica support.

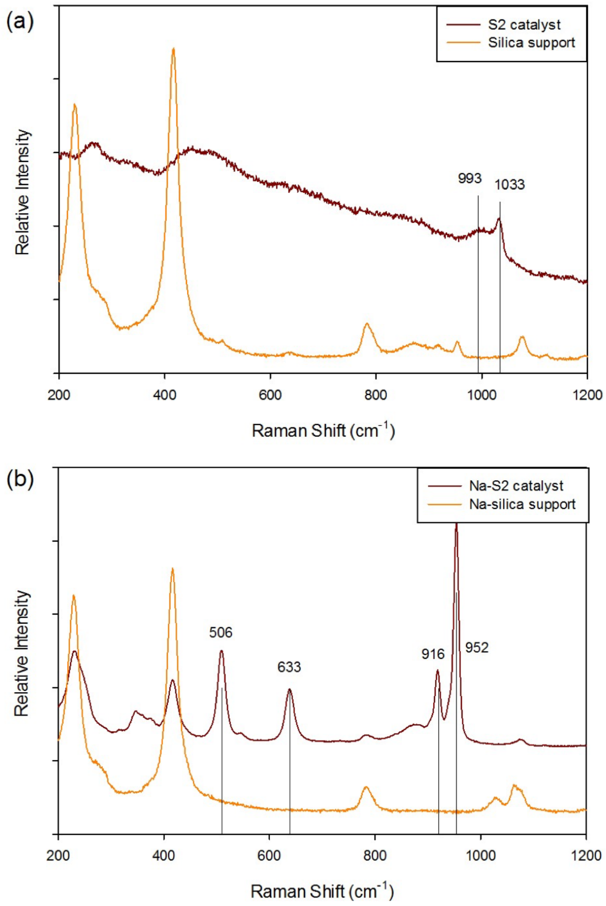

Figure 4. Raman spectra of (top) Na-free and (bottom) Na-promoted S2 catalyst (3.1 V/nm^2) as well as corresponding silica supports.

Raman spectra of the Na-free and Na-promoted silica support and VO_x/SiO_2 catalysts were collected in order to establish the nature of the surface species in these two series of supported vanadia catalysts. Figure 3 shows the Raman spectra of the Na-free and Na-promoted silica supports. Raman shift peaks at 1058 and 1023 cm^{-1} in the spectrum of the Na-bearing silica support (upper spectrum in Fig. 3) are assigned to sodium silicate.[16] Figure 4 shows the Raman spectra of Na-free (a) and Na-promoted S2 (b) catalysts as well as corresponding silica supports. The Raman spectrum of the Na-free S2 catalyst (upper spectrum in Fig. 4 (a)) shows the presence of peaks at 993 and 1033 cm^{-1}, which correspond to the bulk V_2O_5 crystals and V=O bond stretching vibration of the monomeric VO_x species, respectively.[17] The addition of Na resulted in the appearance of Raman peaks at 506, 637, 914 and 950 cm^{-1} associated with presence of Na metavanadate instead of 2D or 3D vanadia.[18] Na metavanadate was previously reported to be inactive in ODH reactions.[16-19] which may explain the lack of catalytic activity of our Na-promoted VO_x/SiO_2 catalysts. According to Irusta et al.,[19] vanadate species react with Na^+ cations present on the surface of the Na-promoted silica forming surface $NaVO_3$-like compounds that were inactive for methane oxidation to formaldehyde. Similar observations were reported by Adamski et al.,[20] that the conversion of propane during its ODH over alkali-doped supported 3V/Zr catalysts decreased in the following order: un-doped > Li^+ > Na^+ > K^+, indicating that alkali dopants were detrimental for the ODH activity of supported vanadia catalysts. Furthermore, we confirmed the carbon deposition in used catalysts by comparing the Raman spectra of fresh and used catalysts. Figure 5 compares the Raman spectra of the fresh and used S4 catalysts after propane ODH in the presence of CO_2 (GHSV = 2500 h^{-1} and $CO_2 : C_3H_8 = 2 : 1$ in He balance at 600°C). The Raman peaks at 993 and 1033 cm^{-1} decreased in intensity due to reduction of VO_x species during the reaction, which represent the stretching mode of monomeric V=O species, while

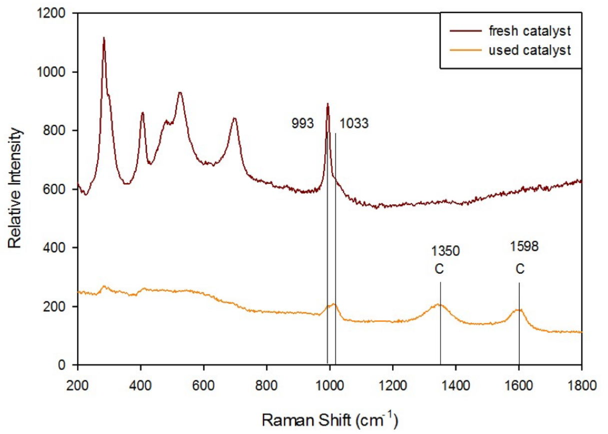

Figure 5. Raman spectra of fresh and used S4 catalysts after propane ODH in the presence of CO_2. (GHSV = 2500 h^{-1} and $CO_2 : C_3H_8 = 2 : 1$, He balance at 600°C).

new peaks were observed at 1350 and 1598 cm^{-1} that correspond to the D and G bands of carbon. The G band represents graphitic carbon and the D band represents disorder within the sp^2 bonded carbon as in Figure 5.[21]

Figure 6 shows the Raman spectra of the Na-free and Na-promoted S4 catalysts containing the highest VO_x loading (6.6 V/nm^2). The Raman V=O stretch is clearly observed at 1028 cm^{-1} in the absence of Na^+ indicating the presence of molecularly dispersed VO_x species. However, this band was broadened as increasing vanadium contents might be due to a higher content microcrystalline V_2O_5 than this feature for the catalysts at lower VO_x coverage. The Raman features of molecularly dispersed VO_x species were absent in the Raman spectrum of the Na-promoted S4 catalyst. Surface Na metavanadate was also expected for this catalyst, although its Raman spectrum lacked strong features associated with Na metavanadate in agreement with previous observations.[16] Improved vanadium dispersion in the presence of Na^+ was further confirmed by EDS elemental mapping. Figure S5 reports the results of elemental mapping for V, Si, O, C and Na on Na-free and Na-promoted S4 catalysts (6.6 V/nm^2) corresponding to the highest V(wt.%) loading investigated in this study. In the absence of Na^+, a large vanadium oxide particle is visible in the center top region of the images shown in Figure S5a confirming that VO_x species form a bulk phase above theoretical monolayer coverage (185.7% in Table 1). In the presence of Na^+, the dispersion of VO_x species is improved significantly manifested in the absence of large vanadium oxide particles (Figure S5b). Increased theoretical monolayer coverage of VO_x in Na-promoted catalysts reduces the V surface coverage in the Na-promoted S4 catalyst to ca. 72.2% of the theoretical monolayer (Table 1). However, while Na promotion improves the dispersion of VO_x species on silica, it results in the formation of surface Na metavanadate species that lack catalytic activity in both propane ODH reactions. The presence of Na^+ is believed to adversely affect the redox behavior of surface VO_x species, which prevents the regeneration of the V^{5+} oxidation state important for propane activation.

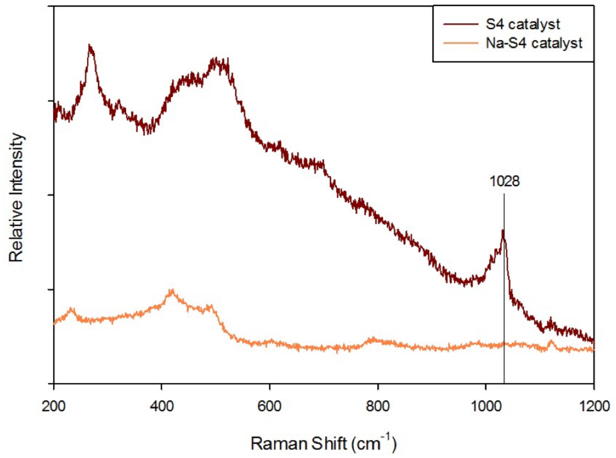

Figure 6. Raman spectra of the Na-free and Na-promoted S4 catalyst (6.6 V/nm^2).

Conclusions

Propane ODH by O_2 and CO_2 was performed over Na-free and Na-promoted supported VO_x/SiO_2 catalysts. The propylene yield was very similar in both CO_2 and O_2 ODH reactions with a maximum value of ca. 11 mol.% observed for the S2 catalyst. However, the propane conversion increased dramatically with vanadium content, e.g., 18 % for O_2 and 9.2% for CO_2 ODH at 1.9 V/nm^2 for the S1 catalyst, while it increased to > 25% at higher VO_x loadings for both O_2 and CO_2 ODH. We observed a trend through Raman study that as increase vanadium content on silica, 2D vanadia structure was formed at first and then as vanadium content increases, 3D vanadia crystalline structure is favorably formed. So that maximum 2D structure of vanadia which shows high activity for CO_2 ODH of propane was obtained in a monolayer coverage range and we confirmed that by calculating TOF rate of propane conversion. Considerable carbon deposition was observed in used catalysts after propane ODH by CO_2, the extent of which correlated with their catalytic activity.

Promotion with Na cations significantly improved the dispersion of surface VO_x species and resulted in the formation of surface Na metavanadate or another reduced V^{3+}/V^{4+} phase, which displayed no catalytic activity in propane ODH in the presence of CO_2.

Experimental Section

A series of VO_x/SiO_2 catalysts were synthesized at different vanadia loadings to study the effect of vanadia surface coverage on conversion and selectivity in propane ODH. Ammonium metavanadate (Sigma-Aldrich, 99% ACS grade) was deposited on a commercial silica support (Saint-Gobain; SS 61138, BET surface area: 261 m^{2}g^{-1}) by incipient wetness impregnation method at 4 different vanadia loadings. After impregnation, the as-synthesized catalysts were dried in a vacuum oven at 60°C for 4 h and then calcined in air at 550°C for 3 h. Also 4 different Na-promoted

VO_x/SiO_2 catalysts were also synthesized at the same vanadia loadings (Table 1). First, Na-promoted silica supports were prepared using sodium nitrate (Fisher Scientific, Certified ACS Grade, >99% purity) by incipient wetness impregnation of the same silica support by a $NaNO_3$ solution. Na loadings were adjusted for different supported vanadia catalysts to yield Na-promoted VO_x/SiO_2 catalysts corresponding to the atomic ratio of Na/V = 0~0.3. Prior to VO_x deposition, as-synthesized Na-promoted silica were calcined in air by ramping the temperature at 1.5°C min^{-1} to 700°C and holding for 4 h. These catalysts were then synthesized following the same procedures described above that were used for the Na-free catalysts. The surface loadings (V/nm^2) and coverages (% of the theoretical monolayer) reported in Table 1 were calculated on the basis of EDS V and Si compositions in these catalysts. The V content (wt. %) was converted to surface loadings (V/nm^2) according to the following formula:

$$\frac{V}{nm^2} = \frac{V(wt.\%)\cdot N_A(\frac{atoms}{mol})}{100(\frac{g}{g})\cdot AW_V(\frac{g}{mol})\cdot S_{BET}(\frac{m^2}{g})\cdot 10^{18}(\frac{nm^2}{m^2})} \qquad (3)$$

These loadings were referenced to theoretical monolayer coverages reported by Grant e al.[16] to yield vanadium surface coverages reported in Table 1.

Oxidative dehydrogenation of propane by O_2 and CO_2 was performed at atmospheric pressure in a continuous flow fixed bed tubular reactor. 0.5 g of different VO_x/SiO_2 catalysts placed between quartz wool plugs inside the reactor (a stainless steel tube of 1/4 inch O.D.) were pre-treated in a flowing O_2/He mixture (10 ml/min each) for 1 h at 450°C prior to the catalytic tests. The feed gas mixture consisted of helium (UHP grade, Wright Brothers, Inc.), carbon dioxide (Tech. grade, Wright Brothers, Inc.) or oxygen (UHP grade, Wright Brothers, Inc.) and propane (CP grade, Matheson gas) at a total flow rate of 16 ml/min to establish the GHSV of 2500 h^{-1}. The O_2 concentration employed in these studies was half of the CO_2 concentration used in ODH reaction to minimize homogeneous oxidation of propane (propane/oxidant ratio of 2:1 for CO_2 and 1:1 for O_2, balance of He), while reaction temperature was varied from 350 to 550°C. The effluent gas was directly passed through the heated sampling valves to online GC-MS system (Shimadzu, GCMS QP-5000) equipped with a capillary column (Supelco, Carboxen 1006 PLOT, Fused silica) of 30 m in length and 0.32 micron film thickness and using ultrapure helium (Wright Brother Inc., Lot 9047-1) as the carrier gas. The products were identified using NIST Mass Spectrum Library 2008 (Shimadzu, No. 225-13290-91). The catalysts were also characterized by TGA (SDT-Q600 unit from TA Instruments, New Castle, DE, USA), and Raman spectroscopy (Horiba T64000, Horiba Scientific, Edison, NJ, USA) equipped with a 514 nm laser line, before and after the ODH of propane reaction. STEM imaging and EDS elemental mapping of the two S4 catalysts corresponding to the highest V surface loading investigated in this study was conducted using the FEI Probe Corrected Titan3™ 80-300 S/TEM.

Acknowledgements

This research was supported by the National Science Foundation under Grant no.OCDO R-12-14.

Keywords: ODH by CO_2 • Selective Oxidation of Propane • Sodium modification of silica • Extend vanadia coverage • Na-metavanadate

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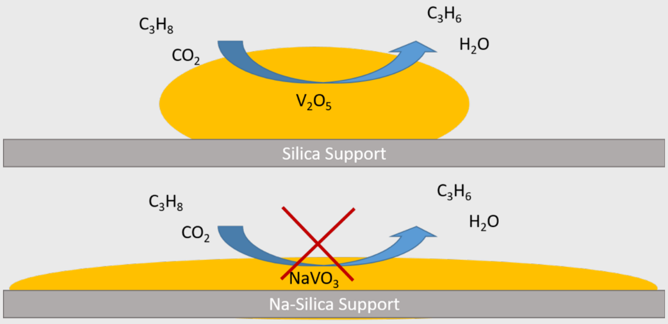

Na addition improves dispersion of vanadia on the silica surface. However, it results in a loss of catalytic activity in propane ODH.

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Carbon Dioxide as Feedstock in Selective Oxidation of Propane