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Oxydehydrogenation of Propane over Vanadyl Ion-Containing VAPO-5 and CoAPO-5

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Vanadyl ion-containing VAPO-5 and CoAPO-5 are prepared by contact with a vanadyl sulfate solution or by impregnation with aqueous vanadyl oxalate and characterized by powder X-ray diffraction, electron spin resonance spectroscopy, and temperature-programmed reduction (TPR). Treatment of VAPO-5 with vanadyl ion results in incorporation of up to 1.0 wt% total vanadium into the AFI framework by filling lattice vacancies. At vanadium contents above ca. 1 wt%, extraframework vanadium is also obtained. TPR results show that framework vanadium can be reduced by hydrogen at a lower temperature than extraframework vanadium and vanadium in bulk V_2O_5. Oxydehydrogenation of propane over VAPO-5 samples reveals that framework vanadium is the most active and selective species for propylene formation (at 400°C and 5% conversion, the selectivity is 72%); extraframework vanadium species are less active and selective. © 2000 Academic Press

Key Words: **propane oxidation; VAPO-5; CoAPO-5; extraframework vanadium.**

1. INTRODUCTION

A large number of mixed metal oxide materials have been investigated as catalysts for the oxydehydrogenation of propane, e.g., V–Mg–O (1, 2), Mg–V–Sb–O (3–5), V–Nb–O (6), *Ln*–V–O (*Ln* = Y, Ce, Yb) (7), Mg–Mo–O (8), and *M*–Mo–O (*M* = Ni, Co, etc.) (9, 10). Vanadium appears to be one of the key elements in oxide-based catalysts for oxydehydrogenation whether it is contained in the bulk of the solid or supported on oxide surfaces (11). Molecular sieve materials containing framework vanadium have been reported as catalysts for oxydehydrogenation of propane (12–15). Vanadium-containing aluminophosphate VAPO-5 was shown to be a selective catalyst, giving propylene with selectivities around 70% for conversions around 15% at 500°C (12, 14). Additionally, Centi and Trifiro have reported that vanadium-containing zeolites prepared by hydrothermal methods can have high selectivity for propylene (76% at 4% conversion at 408°C) (15).

While the redox properties of the vanadium species in VAPO-5 have been investigated (16–21), it is not completely clear whether vanadium framework sites are the most active and selective for propylene formation. In this work, vanadium is introduced into VAPO-5 and CoAPO-5 by contact with a vanadyl sulfate solution or impregnation with aqueous vanadyl oxalate, and the resulting materials are examined as catalysts for propane oxidation in order to address the following questions: (i) Under what conditions are framework and/or extraframework vanadium species generated? (ii) Does framework vanadium behave differently from extraframework vanadium?

2. EXPERIMENTAL SECTION

2.1. *Catalyst Preparation*

VAPO-5 was synthesized by a method that was modified from our previous work (16). First, 25.3 g of phosphoric acid (85%, Mallinckrodt) diluted by 18 ml of water was added to a slurry of 15.7 g of pseudoboehmite (Catapal B, Vista Chemical Co.) in 57.6 ml of water. The resultant white viscous gel was stirred at room temperature for 90 min and then 1.1 g of vanadium(V) oxide (Aldrich) was added. After the mixture was stirred for 20 min, 24.5 ml of triethylamine (J. T. Baker) was added and the mixture was homogenized at room temperature for 90 min. The final gel composition was 1.5 $Et_3N : Al_2O_3 : 0.95\ P_2O_5 : 0.05\ V_2O_5 : 40\ H_2O$. The gel was heated in a Teflon-lined autoclave at 200°C and autogenous pressure. The product slurry containing VAPO-5 crystals was stirred and allowed to settle in a beaker. The crystals at the bottom of the beaker were collected. After water was added to the crystals, the slurry was stirred and settled again. This procedure was repeated several times until a clear supernatant was obtained, in order to remove unreacted, colloidal, amorphous alumina. To synthesize VAPO-5 with high vanadium content, vanadyl sulfate (Aldrich) was used instead of vanadium(V) oxide (18).

As-synthesized VAPO-5 was calcined in dry air at 550°C for 6 h to remove the organic template. Calcined VAPO-5

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was reduced in a 100% hydrogen stream at 500°C for 3 h. After reduction, contact of VAPO-5 (1.2 g) with a vanadyl sulfate solution (0.024 M, 200 ml) was carried out at room temperature for 1 day twice. Alternatively, the reduced VAPO-5 (1.6 g) was added to 2 ml of an aqueous solution of vanadyl oxalate (90 mg, GFS Chemicals), and then dried using a rotary evaporator to prepare an impregnated VAPO-5.

CoAPO-5 was prepared according to our previously reported procedure (22). Cobalt(II) sulfate (Aldrich) was used as the cobalt source. The starting gel composition was 1.5 Et_3N : 0.95 Al_2O_3 : P_2O_5 : 0.05 Co_2O_3 : 40 H_2O. As-made CoAPO-5 was calcined, reduced, and vanadyl ion-treated in the same manner as VAPO-5.

SAPO-5 and $AlPO_4$-5 were obtained by hydrothermal syntheses from gels of 1.5 Et_3N : Al_2O_3 : 0.95 P_2O_5 : 0.1 SiO_2 : 40 H_2O and 1.5 Et_3N : Al_2O_3 : P_2O_5 : 40 H_2O molar ratio, respectively. Fumed silica (CAB-OSIL M-5, Cabot Corp.) was used as the silicon source. As-made SAPO-5 and $AlPO_4$-5 were calcined at 550°C for 6 h. Next, 1.2 g of calcined SAPO-5 was contacted with vanadyl sulfate solution (0.024 M, 200 ml) at room temperature for 1 day twice. Finally, 1.6 g of calcined $AlPO_4$-5 was impregnated with 90 mg of vanadyl oxalate in 2 ml of water using a rotary evaporator.

2.2. *Characterization*

X-ray diffraction (XRD) powder patterns were collected on a Scintag XDS-2000 diffractometer using Cu$K\alpha$ radiation.

Elemental analyses were obtained from Galbraith Laboratories, Inc., for all elements reported except for phosphorus. The ratio of phosphorus to aluminum was analyzed by X-ray fluorescence (Kevex 700 IXRF).

Electron spin resonance (ESR) spectra were recorded on an E-line Varian spectrometer at liquid helium temperature. The spectrometer was operated at X-band wavelength with 100 kHz magnetic field modulation. DPPH was used as standard for determining g values. The treated samples were prepared in a flow reactor, transferred into an ESR tube in the glove box, and then sealed.

Temperature-programmed reduction (TPR) was performed in a homemade system equipped with a thermal conductivity detector. Before the TPR measurement, samples were treated in an air stream at 350°C for 2 h (except for the reduced sample, which was treated at 500°C for 3 h in a hydrogen stream), and cooled to 50°C. The flow was changed to a mixture of 8.7% hydrogen and 91.3% nitrogen at 50°C and then the temperature increased at 10°C min^{-1} to 900°C.

2.3. *Propane Oxidation*

Samples were pelletized and sieved to $+250/-417$ μm. A mixture of 0.2–2.0 ml of catalyst and the same volume of silicon carbide was charged into a stainless steel reactor (i.d. 8 mm) in a fixed-bed, atmospheric flow reactor system. The reactor was connected to a gas chromatograph by stainless steel tubing that was heated to 120°C. Product analyses were performed using a gas chromatograph (Hewlett Packard G1800B) equipped with a mass ionization detector and capillary column. The oxydehydrogenation of propane was carried out at 400°C at a mole ratio of propane : oxygen : helium = 4 : 2 : 9. The propane conversion was maintained at 5% by changing the contact time. Gaseous products were analyzed using online sampling, while liquid products were collected in an ice trap, mixed with 1,4-dioxane as internal standard, and injected into the gas chromatograph.

3. RESULTS AND DISCUSSION

3.1. *Catalyst Characterization*

All the AFI-type materials discussed here reveal XRD patterns indicative of highly crystalline materials in their as-synthesized and treated forms. As shown previously (16), the lack of vanadium removed by numerous washings and contact with solutions containing exchangeable ions, e.g., NH_4^+, combined with N_2 adsorption data that are the same as those for $AlPO_4$-5 together provide strong evidence that the vanadium in the VAPO-5 is in the framework. All samples listed here as VAPO-5 have been tested by these criteria and thus have framework vanadium.

Table 1 summarizes the chemical compositions of the synthesis gels and the obtained products. The vanadium content of calcined VAPO-5 is much smaller than that of the starting gel. When vanadium(V) oxide is used as a vanadium source, only 18% of vanadium is incorporated into the VAPO-5. On the other hand, when vanadyl sulfate

TABLE 1

Composition of Catalysts

VAPO-5	Gel (Al : P : V)	Bulk (Al : P : V)	V wt%
Calcined[a]	1 : 0.95 : 0.05	1 : 0.938 : 0.009	0.38
Ion treated[a]	—	1 : 0.913 : 0.022	0.90
VOC_2O_4-impregnated	—	1 : 0.920 : 0.051	2.1
Calcined[b]	1 : 0.95 : 0.05	1 : 0.926 : 0.022	0.90
CoAPO-5	Gel (Al : P : Co)	Bulk (Al : P : Co : V)	V wt%
Calcined	0.95 : 1 : 0.05	0.966 : 1 : 0.052	—
Ion treated	—	0.937 : 1 : 0.045 : 0.002	0.06
SAPO-5	Gel (Al : P : Si)	Bulk (Al : P : Si : V)	V wt%
Calcined	1 : 0.95 : 0.05	1 : 0.895 : 0.052	—
Ion treated	—	1 : 0.925 : 0.049 : 0.005	0.21
$AlPO_4$-5	Gel (Al : P)	Bulk (Al : P : V)	V wt%
Calcined	1 : 1	1 : 0.991	—
VOC_2O_4-impregnated	—	1 : 0.994 : 0.042	1.7

[a] Vanadium(V) oxide was used as a vanadium source.

[b] Vanadyl sulfate was used as a vanadium source.

is employed, the vanadium utilization is about 50%. Vanadium substitutes for phosphorus in the framework of VAPO-5 (16). However, for the calcined VAPO-5 samples made from either vanadium(V) oxide or vanadyl sulfate, the aluminum content is larger than the sum of phosphorus and vanadium, suggesting that the calcined VAPO-5 materials contain amorphous alumina and/or phosphorus defect sites. After ion treatment, the vanadium content increases to more than twice the value of the as-made material. For the case of CoAPO-5, cobalt replaces framework aluminum (22). The sum of aluminum and cobalt is almost equal to the phosphorus content in the calcined CoAPO-5. These data suggest that pure, defect-free CoAPO-5 is formed. Chemical analysis of SAPO-5 suggests that the sample may contain amorphous alumina.

The ESR spectra of VAPO-5 samples recorded at liquid helium temperature (4 K) are shown in Fig. 1. The spectrum of as-made VAPO-5 is similar to that reported previously (16–21) and is characterized by two axially symmetric signals due to V^{4+} ions with hyperfine splitting that is caused by interaction between the unpaired $3d^1$ electron and the ^{51}V nucleus ($I = \frac{7}{2}$, natural abundance = 99.8%). The two sets of ESR parameters are $g_{\|} = 1.948$, $A_{\|} = 196$ G, $g_{\perp} = 1.997$, $A_{\perp} = 78$ G (species 1), and $g_{\|} = 1.949$, $A_{\|} = 189$ G (species 2). These values are typical for V^{4+} in a vanadyl species with distorted octahedral coordination (23). Recently Prakash and Kevan have reported that the signals from species 1 and 2 can be assigned to a vanadyl species with three water ligands and a vanadyl species containing two water ligands and a hydroxyl ligand (21). After calcination of the sample at 550°C for 5 h, the signal intensity significantly decreases because of the oxidation of V^{4+} to V^{5+}. However, a small amount of V^{4+} remains and is still highly dispersed after calcination (species 3). Reduction at 500°C for 3 h in 100% hydrogen increases the signal intensity and gives the same parameters as calcined VAPO-5. Since high-temperature reduction removes water, species 3 may be dehydrated V^{4+} in the AFI framework. In general, the amount of V^{4+} observed by ESR was in the neighborhood of one-third that from the bulk elemental analysis. Although this is not an exact agreement it is reasonable in view of the errors involved in the analysis. After treatment of VAPO-5 with the vanadyl sulfate solution, the resultant spectrum shows only the signal of species 1, with increased intensity. These data strongly suggest that the added vanadium is incorporated into the VAPO-5 framework during the ion treatment. Upon heating of the ion-treated VAPO-5, species 1 is converted to dehydrated V^{4+} (species 3).

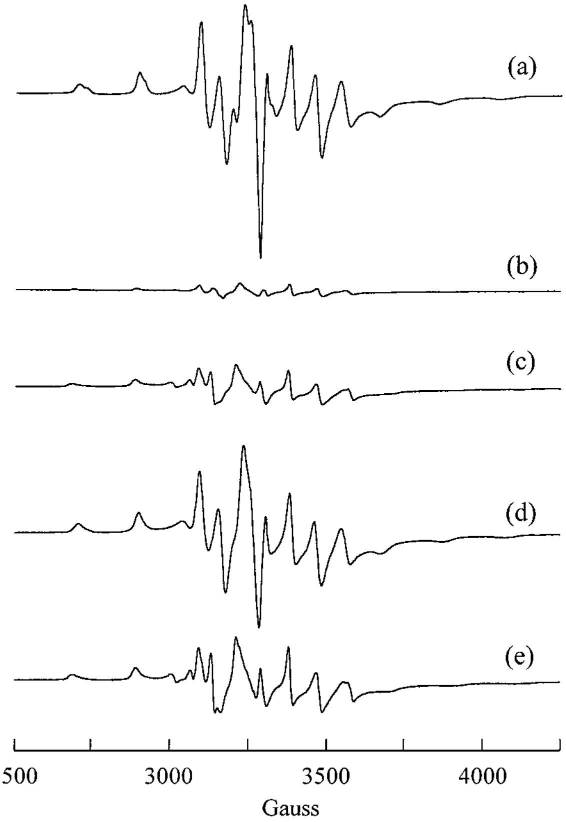


FIG. 1. Electron spin resonance spectra of VAPO-5 samples (a) as-synthesized, (b) calcined at 550°C for 5 h in air, (c) reduced at 500°C for 3 h in hydrogen stream after (b), (d) treated with vanadyl sulfate solution after (c), and (e) heated at 350°C for 2 h in nitrogen stream after (d). Samples for (b), (c), and (e) were treated in a flow reactor, transferred into an ESR tube in a glove box, and the tubes sealed before analysis.

Figure 2 shows the ESR spectra of VAPO-5 and $AlPO_4$-5 impregnated with vanadyl oxalate. The ESR spectrum of impregnated VAPO-5 consists of two signals: a very broad singlet and a hyperfine signal superimposed on the broad singlet. The hyperfine signal is due to framework vanadium coordinated by water since the ESR parameters are identical to those of species 1. Appearance of a broad singlet signal suggests the formation of small vanadium clusters because of the vanadium–vanadium interaction. Thus, impregnation of vanadium into VAPO-5 results in the formation of extraframework vanadium clusters (species 4). Comparing the ESR signals from the vanadyl ion-treated and impregnated VAPO-5, the intensity of the hyperfine signals after subtraction of the broad singlet (Fig. 2a) is almost equal to the signal intensity of the sample shown in Fig. 1d. As mentioned above, the treatment with vanadyl ion introduces vanadium into the framework. Table 1 shows data that suggest that up to 0.9 wt% of vanadium can be incorporated into the framework by ion treatment. After impregnation, the intensity of the hyperfine peaks increases to that of ion-treated VAPO-5, indicating that during the impregnation, vanadium is incorporated into the framework to 0.9 wt% and that the excess amount of vanadium forms extraframework vanadium species. Some incorporation of vanadium into the $AlPO_4$-5 framework also occurred during impregnation, as the spectrum from impregnated $AlPO_4$-5 (Fig. 2b) shows a hyperfine

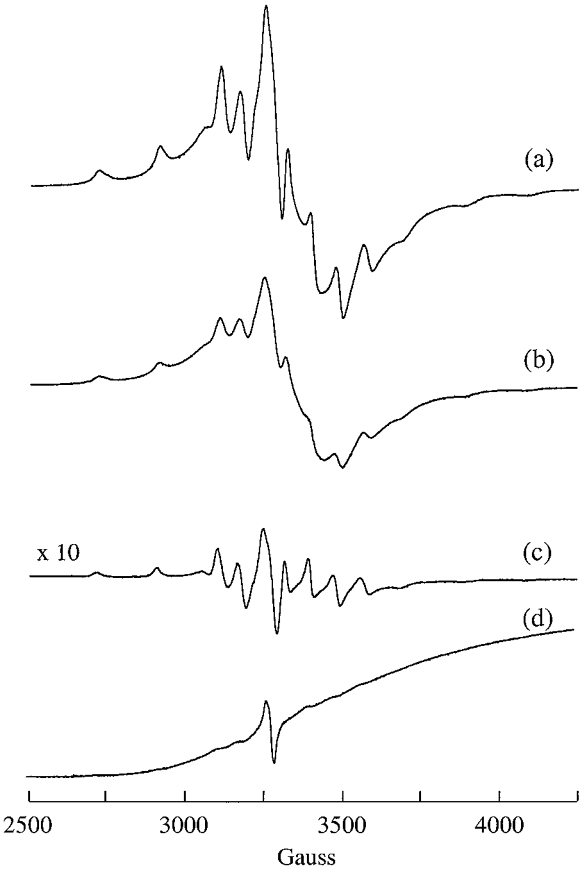


FIG. 2. Electron spin resonance spectra of (a) VAPO-5 impregnated with vanadyl oxalate, (b) $AlPO_4$-5 impregnated with vanadyl oxalate, (c) SAPO-5 treated with vanadyl sulfate solution, and (d) CoAPO-5 treated with vanadyl sulfate solution.

signal indicative of framework vanadium as well as a broad signal.

The ESR spectrum from vanadyl ion-treated SAPO-5 (Fig. 2c) shows only the hyperfine signal of species 1. This would suggest that the vanadium is incorporated into the framework of SAPO-5. However, as shown below, the TPR and catalytic results are not necessarily consistent with this interpretation. Alternatively, the vanadium could be in ion-exchange positions. The ESR spectrum of VO^{2+} exchanged in zeolite beta (not shown) is similar, so that framework and ion-exchanged vanadium may not be distinguishable by ESR. The spectrum of vanadyl ion-treated CoAPO-5 shows a weak hyperfine signal, whose parameters are equal to those of the hyperfine signal of framework vanadium in VAPO-5.

Temperature-programmed reduction (TPR) results are shown in Fig. 3. For the calcined VAPO-5 (Fig. 3a), two peaks are observed at 420°C and 520°C. The TPR spectrum of VAPO-5 has been reported previously by Concepción *et al.* (13). They obtained only one peak at 470–475°C. It is possible that our TPR system has higher resolution and is able to resolve two desorptions in the temperature range of 420–520°C. At this time we are unable to conclusively assign the two reduction events. A sample reduced in 100% hydrogen at 500°C for 2 h gave no peaks in the TPR spectrum (Fig. 3b). After vanadyl ion treatment, the two peaks appeared again in the TPR, and the peak intensity at 520°C is twice as large as that in the original calcined sample. Since there is no change in the peak position of the reduction, the added vanadium is likely in the framework. The spectrum of VAPO-5 impregnated with vanadyl oxalate is shown in Fig. 3d. Impregnated VAPO-5 has both framework and extraframework vanadium, according to ESR; the larger TPR peak is shifted to 545°C, higher than the reduction temperature for framework vanadium. The peak at 545°C is most likely a superposition of two peaks due to reduction of framework and extraframework vanadium. Vanadium in SAPO-5 treated with the vanadyl sulfate solution is reduced at 540°C (Fig. 3e). The TPR of $AlPO_4$-5 impregnated with vanadyl oxalate gives one strong reduction peak at 590°C that is assigned to the reduction of

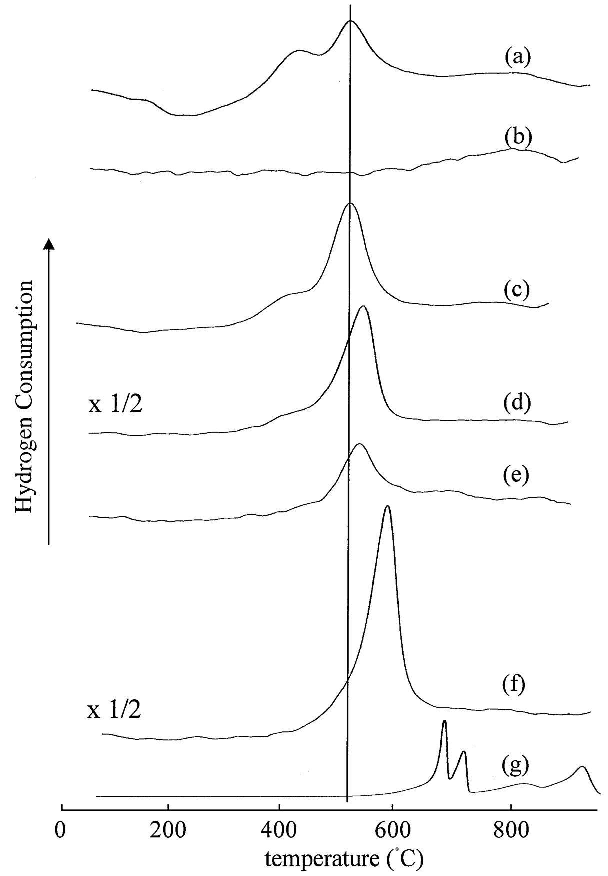


FIG. 3. Temperature-programmed reduction spectra of VAPO-5 samples (a) calcined at 550°C for 5 h in air, (b) reduced at 500°C for 3 h in hydrogen stream after (a), (c) treated with vanadyl sulfate solution after (c), and (d) impregnated with vanadyl oxalate after (b), (e) SAPO-5 treated with vanadyl sulfate solution, and (f) $AlPO_4$-5 impregnated with vanadyl oxalate and (g) vanadium(V) oxide.

TABLE 2

Amount of Hydrogen Consumed in the TPR Experiment (mol/g)

	Vanadium content[a]	Amount of H_2 consumed[b] (×2)
Calcined VAPO-5	7.5×10^{-5}	9.2×10^{-5}
VO/VAPO-5[c]	1.8×10^{-4}	1.5×10^{-4}
VOC_2O_4/VAPO-5[d]	4.1×10^{-4}	2.0×10^{-4}
VO/SAPO-5[c]	4.1×10^{-5}	2.9×10^{-5}
$VOC_2O_4/AlPO_4$-5[d]	3.3×10^{-4}	1.5×10^{-4}
VO/CoAPO-5[c]	1.2×10^{-5}	1.5×10^{-5}

[a] Calculated using elemental analysis data from Table 1.

[b] Total amount from all peaks (except, for VO/CoAPO-5, only the peak at 520°C).

[c] Treatment with vanadyl sulfate solution.

[d] Impregnation with vanadyl oxalate.

extraframework vanadium. The ESR spectrum of the impregnated $AlPO_4$-5 reveals that a small amount of vanadium is in the framework. However, no reduction peak from the framework vanadium is observed, most likely because it is below the detection limits. Bulk vanadium oxide, V_2O_5 (Fig. 3g), shows a TPR spectrum considerably different from those of VAPO-5 and $AlPO_4$-5; all four peaks are above 650°C, in agreement with reported data (24). TPR results indicate that framework vanadium is the most reducible species among the samples investigated; the order of vanadium reducibility by hydrogen is framework vanadium > isolated extraframework vanadium > clustered extraframework vanadium > bulk vanadium oxide.

Table 2 shows a summary of the hydrogen consumption. All the samples were pretreated in air before measurement. Almost all the vanadium in the samples is likely to be in the 5+ state after the oxidation as evidenced by the ESR spectra. Up to 1 mol of H_2 per 2 mol of V is consumed; these results indicate that vanadium 5+ can be reduced to 4+, and that reduction to 3+ most likely does not occur to any significant extent.

Figure 4 shows the TPR results from CoAPO-5 samples. In the spectrum of calcined CoAPO-5 (Fig. 4a), there is a strong peak above 650°C assigned to reduction of framework cobalt with structural decomposition. After ion treatment, a new weak peak appears at 520°C. This temperature is equal to the reduction temperature of framework vanadium in VAPO-5. The amount of hydrogen consumed (Table 2) strongly suggests that the peak at 520°C is due to vanadium reduction and that vanadium is present in the framework of CoAPO-5.

3.2. *Propane Oxidation*

3.2.1. Comparing molecular sieve samples. The oxydehydrogenation of propane was carried out at 400°C with a mole ratio of propane : oxygen : helium = 4 : 2 : 9. The propane conversion was maintained at 5% by changing the contact time. The reaction results are summarized in Table 3. The main products are propylene, CO, and CO_2, while no oxygenates are formed. VAPO-5 is active and selective for propane oxydehydrogenation, as reported by Concepción *et al.* (12, 13) and Salem *et al.* (14). Propane conversion reached 5% at a short contact time (0.47 s) and the selectivity for propylene was 72%. Over vanadyl ion-treated VAPO-5, the product distribution is the same as that from calcined VAPO-5, suggesting the same active site; i.e., vanadium is incorporated into the framework during the ion treatment. Rigutto and Bekkum have used vanadyl sulfate as vanadium source to prepare VAPO-5 and synthesized a relatively high vanadium content VAPO-5 (18). Comparing the reaction results over (1) VAPO-5 treated with the vanadyl ion and (2) VAPO-5 prepared by hydrothermal synthesis using vanadyl sulfate, with both containing the same total content of vanadium, 0.90 wt%, the product distribution and (within experimental error) contact times are the same. Thus, these data along with the ESR and TPR results indicate incorporation of vanadium into the framework during ion treatment. The rates of propane consumption per vanadium atom (total vanadium by elemental analysis) are 0.017 and 0.015 s^{-1} for VAPO-5 (0.38 wt%) and VAPO-5 (0.9 wt%), respectively (data from Table 2), and over a temperature range of 350–450°C give an apparent activation energy of 98 kJ/mol.

When vanadium levels above 0.9 wt% are achieved by impregnation of vanadyl oxalate, both activity and propylene selectivity are depressed. These results, along with

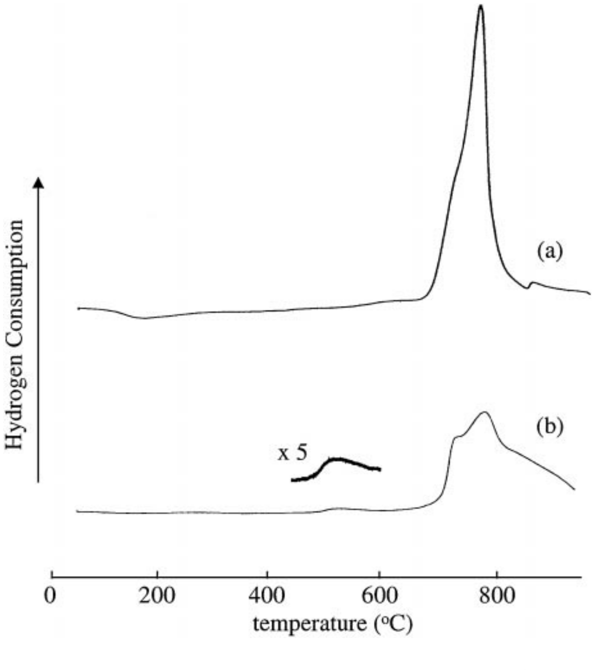


FIG. 4. Temperature-programmed reduction spectra of CoAPO-5 samples (a) calcined at 550°C for 5 h in air and (b) treated with vanadyl sulfate solution after reduction at 500°C for 3 h in hydrogen stream.

TABLE 3

Selectivity at 5% Propane Conversion

Catalyst	V content (wt%)	Selectivity: Propylene	Ethylene	C_6H_6	CO	CO_2	Contact time (s)
VAPO-5[a]	0.38	72.0	0.5	0	18.4	9.1	0.47
VO/VAPO-5[a,c]	0.90	73.0	0.6	0	17.8	8.6	0.30
VAPO-5[b]	0.90	72.0	0	0	19.3	8.8	0.22
CoAPO-5	0	18.6	2.6	4.8	28.6	45.4	5.3
VO/CoAPO-5[c]	0.06	26.9	2.3	3.9	25.3	41.6	3.1
VOC_2O_4/VAPO-5[a,d]	2.1	66.3	0	0	22.5	11.2	0.86
VO/SAPO-5[c]	0.21	29.7	3.4	1.8	35.2	29.9	9.4
VOC_2O_4/$AlPO_4$-5[d]	1.7	58.2	0.3	0	25.2	16.2	3.6

[a] Prepared using V_2O_5.

[b] Prepared using vanadyl sulfate.

[c] Treatment with vanadyl sulfate solution.

[d] Impregnation with vanadyl oxalate. Reaction temperature was 400°C. Propane : oxygen : helium = 4 : 2 : 9.

the ESR and TPR data, indicate that up to approximately 1 wt% total vanadium can be incorporated into the framework, and that additional amounts result in extraframework species that are detrimental to the oxydehydrogenation of propane. Similarly, vanadyl oxalate-impregnated $AlPO_4$-5 shows low catalytic activity and low selectivity for propylene; most of the vanadium in this sample exists as extraframework clusters (rate per total vanadium atom is 2.7×10^{-4} s^{-1}). Thus, extraframework species alone are less active than framework vanadium. The catalytic activity of impregnated VAPO-5 (2.1 wt%) is lower than that of the original VAPO-5, suggesting that extraframework species may block access to framework sites. Additionally, vanadyl ion-treated SAPO-5 has low activity and low selectivity, although the total vanadium content is relatively low, suggesting that the vanadium species in this sample are not in the framework. Taken in total, the reaction results strongly support the conclusion that framework vanadium is the most active and selective catalyst for propane oxydehydrogenation.

Arena *et al.* have reported the relationship between the activity of supported V_2O_5 catalyst in propane oxydehydrogenation and the reducibility of vanadium in TPR (25). Our results of TPR and the activity in propane oxidation are in agreement with their report: the most reducible vanadium species, framework vanadium, is the most active for propane oxidation.

The data presented thus far suggest that framework vanadium (isolated) is more active and selective for oxidative dehydrogenation (ODH) of propane than nonframework and presumably nonisolated vanadium. On supported vanadia catalysts the rates (per V atom) of propane ODH have been shown to be higher for polyvanadate structures than for vanadate monomers (11). It is not possible to directly compare the VAPO-5 solids to the supported vanadia materials. However, several issues can be addressed. First, the existence of tetrahedral framework V^{5+} in VAPO-5 (16) is a state for vanadium that cannot be achieved in supported vanadia catalysts. The environment of vanadate monomers on supported catalysts is almost certainly quite different from that of the V^{5+} state in VAPO-5. Second, the VOC_2O_4/$AlPO_4$-5 would be the most similar to the more isolated species on the supported catalysts. Using an activation energy of 100 kJ/mol and first-order dependence of propane on the rate of ODH, our data give an ODH rate of 0.2×10^{-4} s^{-1} at 333°C, which is in agreement with that of Khodakov *et al.* (11) for very isolated monovanadate species. Our value of around 0.001 s^{-1} at 333°C for VAPO-5 more resembles the data of Khodakov *et al.* (11) for polyvanadate species, but this comparison may not be meaningful for the reasons stated above.

CoAPO-5 shows lower activity and very low selectivity for propylene. Over CoAPO-5 and vanadyl ion-treated CoAPO-5, a small amount of benzene is formed from propylene because of the Brønsted acid sites. Treatment of CoAPO-5 with vanadyl ion slightly improved activity and selectivity, most likely because of incorporation of vanadium in the framework.

3.2.2. Effect of reaction conditions.

The sample of VAPO-5 prepared by hydrothermal synthesis using vanadyl sulfate as a vanadium source, which is the most active and selective material among the catalysts tested, was used to examine the effects of reaction conditions.

Figure 5 shows the effect of changing contact time. The selectivity for propylene increases with decreasing contact time. The selectivity reached 79% at 0.1 s of contact time, but propane conversion is very low (1.2%). Figure 6 shows the relationship between the selectivity and the conversion as a function of oxygen pressure. The propane pressure

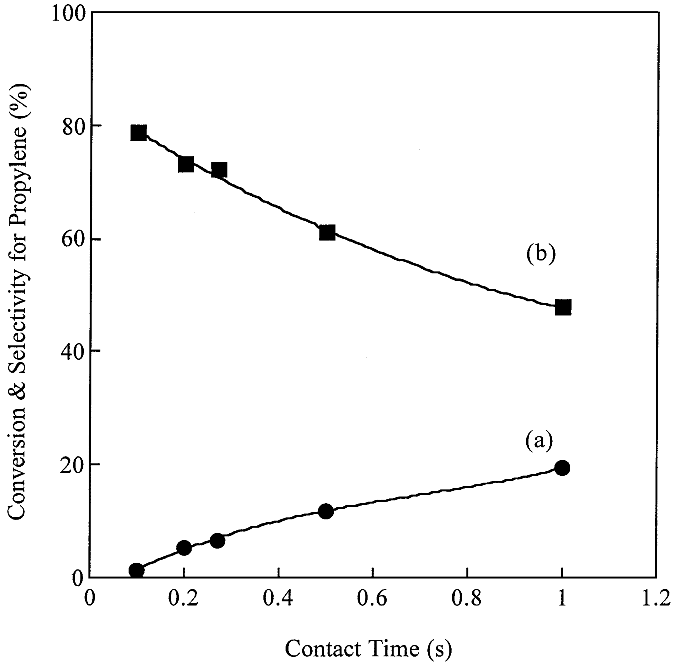


FIG. 5. Effect of contact time on (a) propane conversion and (b) propylene selectivity in partial oxidation of propane over VAPO-5 synthesized using vanadyl sulfate (vanadium content, 0.90 wt%). Reaction temperature was 400°C. Propane, oxygen, and helium pressures were 27.0, 13.5, and 60.8 kPa, respectively.

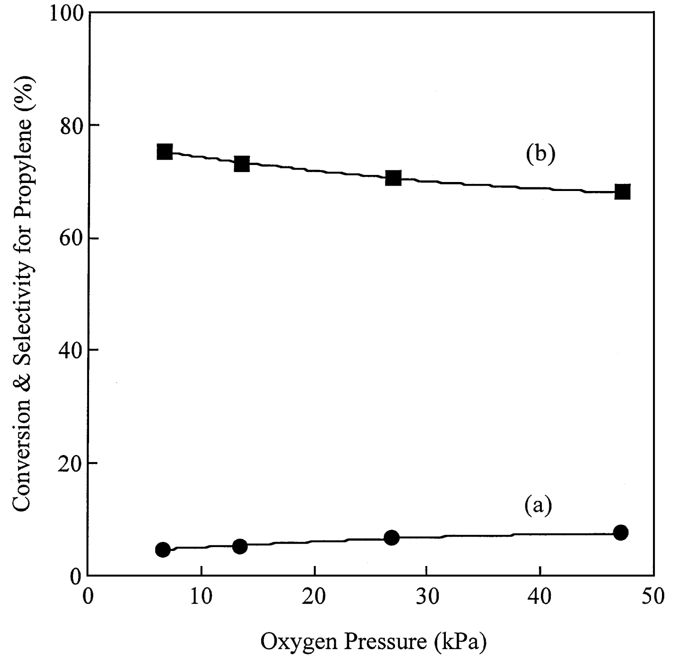


FIG. 6. Effect of oxygen pressure on (a) propane conversion and (b) propylene selectivity in partial oxidation of propane over VAPO-5 synthesized using vanadyl sulfate (vanadium content, 0.90 wt%). Reaction temperature was 400°C. Contact time was 0.20 s. Propane pressure was 27.0 kPa.

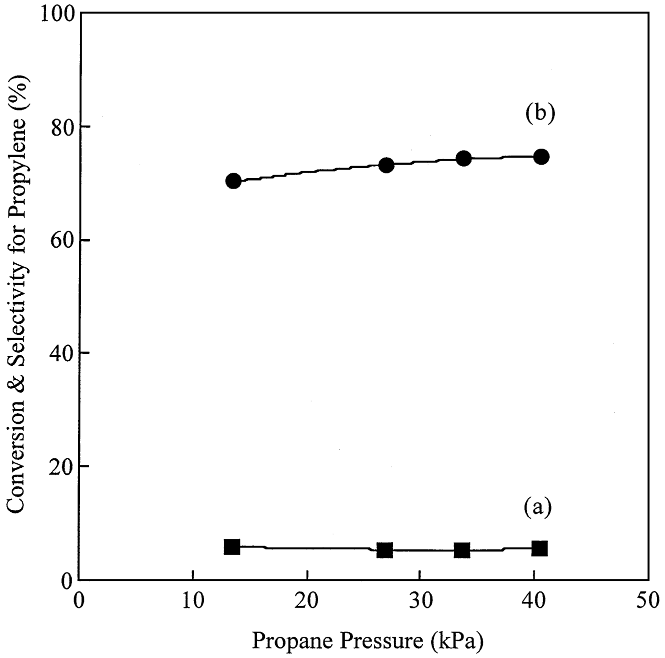
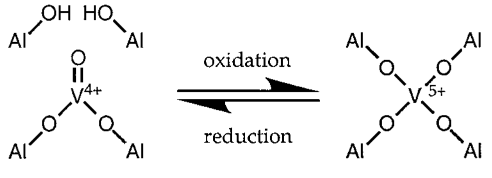


FIG. 7. Effect of propane pressure on (a) propane conversion and (b) propylene selectivity in partial oxidation of propane over VAPO-5 synthesized using vanadyl sulfate (vanadium content, 0.90 wt%). Reaction temperature was 400°C. Contact time was 0.20 s. Oxygen pressure was 13.5 kPa.

was held constant at 27.0 kPa. The oxygen pressure did not affect the selectivity and the conversion to any significant extent. Propylene selectivity increases slightly with increasing propane pressure at 13.5 kPa of oxygen pressure (Fig. 7). Additionally, the conversion is not changed at various propane pressures. Reaction temperature affects both the selectivity and the conversion as shown by the data in Fig. 8. At 350°C, propylene is obtained with 86% selectivity. High selectivity for oxydehydrogenation can be obtained with over 80% selectivity at a low temperature and at a low contact time. However, under these reaction conditions propane conversion is very low.

3.3. *Effect of Added Sodium*

Previously, we speculated that the environment of the vanadium species in the oxidized and reduced forms of VAPO-5 was as follows (16):



The data presented here are consistent with the suggestion that this tetrahedral framework V^{5+} is the most easily reduced form of V^{5+} and the species responsible for

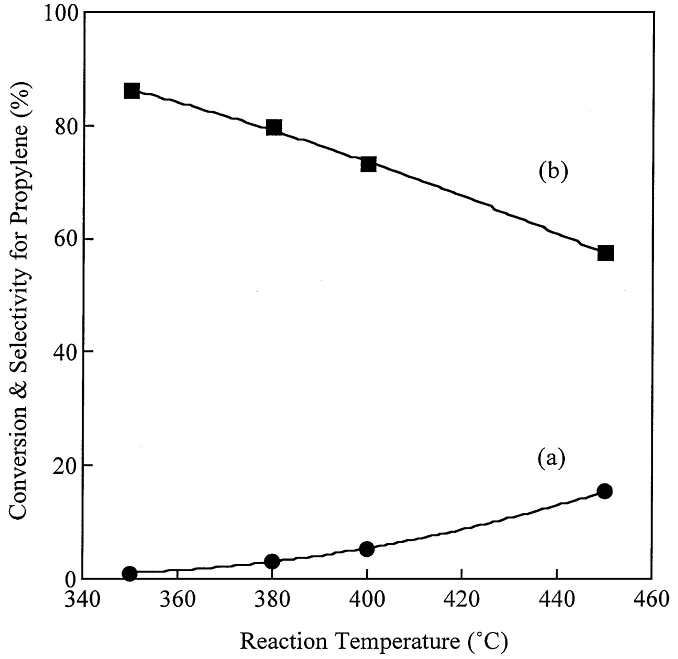


FIG. 8. Effect of reaction temperature on (a) propane conversion and (b) propylene selectivity in partial oxidation of propane over VAPO-5 synthesized using vanadyl sulfate (vanadium content, 0.90 wt%). Contact time was 0.20 s. Propane, oxygen, and helium pressures were 27.0, 13.5, and 60.8 kPa, respectively.

selective propane oxydehydrogenation. As a further test, we attempted to hinder the ability to reach this state according to the above equation, by changing the AlOH groups with Na^+ to give Al-ONa.

A calcined and reduced sample of VAPO-5 is contacted with a 0.1 M sodium chloride solution at room temperature for 2 days to generate Na/VAPO-5. The sodium content of the resultant material is 1.0 wt%, which on a molar basis is 7.5 times larger than the vanadium content (0.30 wt%), indicating that sodium is physically adsorbed on VAPO-5 as well as ion-exchanged. The TPR spectrum of Na/VAPO-5 is shown in Fig. 9. The peak from the framework vanadium in VAPO-5 at 520°C disappears and two peaks appear at 580°C and 660°C. This change is partially reversible: after treatment of Na/VAPO-5 with 0.1 M ammonium chloride solution at room temperature for 2 days, the peak indicative of framework vanadium appears again, while the peak at 580°C increases in area and the peak at 660°C declines in size. Since sodium is not completely removed by this back-exchange (residual sodium content is 0.38 wt%), the two peaks above 580°C still remain.

TABLE 4

Effect of Sodium Cation

Catalyst	Na content (wt%)	Selectivity				Contact time (s)
		Propylene	Ethylene	CO	CO_2	
VAPO-5	0	68.0	1.0	20.9	10.1	1.0
Na/VAPO-5^a	1.0	22.6	0.6	26.3	50.5	7.8
NH_4-Na/ VAPO-5^b	0.38	66.0	1.4	22.3	10.3	3.2

[a] Treatment of reduced VAPO-5 with sodium chloride.

[b] Treatment with ammonium chloride solution after sodium treatment. Vanadium content was 0.3 wt%. Propane conversion was 5%. Reaction temperature was 400°C. Propane : oxygen : helium = 4 : 2 : 9.

Table 4 shows the effect of sodium cation on propane oxidation. Over Na/VAPO-5, the activity and the selectivity for propylene are very low. After the treatment with ammonium chloride solution, the activity increases and the selectivity is recovered to values approaching those of the original VAPO-5. These findings, especially the reversibility of the effect, support the proposal that the interconversion shown above is involved in generation of the active, selective oxydehydrogenation sites, and that the presence of AlOH groups is essential to its facility.

An alternate interpretation, that might contribute to the sodium effect, is extraction of some vanadium from the

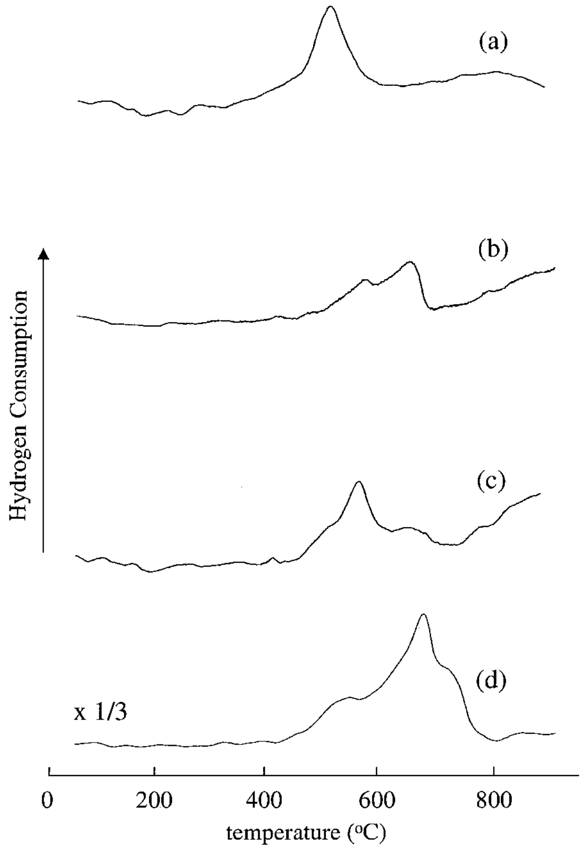


FIG. 9. Effect of sodium ion on temperature-programmed reduction spectra for (a) samples calcined at 550°C for 5 h in air, (b) treatment of reduced VAPO-5 with sodium chloride solution, (c) treatment with ammonium chloride solution after (b), and (d) impregnation of calcined $AlPO_4$-5 with sodium metavanadate. Before measurement, all samples were calcined at 350°C for 1 h in a dry air stream.

framework by interaction with sodium at the reaction temperature of 400°C. Figure 9 also shows the TPR spectrum of $AlPO_4$-5 impregnated with sodium metavanadate (Na, 1.0 wt%). The main peak is at 690°C, similar to the peak from Na/VAPO-5. This result suggests the possibility that some extraframework vanadium is generated in the latter sample, which could be a partial cause of the changes in catalytic properties. At present we cannot assess the relative importance of these two explanations.

4. CONCLUSIONS

Framework vanadium in aluminophosphate-based molecular sieves with the AFI topology is the most active and selective vanadium species for propane oxydehydrogenation. Treatment of VAPO-5 with vanadyl sulfate solution enhances the catalytic activity because vanadium is incorporated into the VAPO-5 framework during ion treatment. Vanadium levels above 1 wt%, achieved by impregnation, result in the formation of extraframework vanadium, which is less active and less selective and may also block access to framework active sites.

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