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Oxidative Dehydrogenation of Methanol Catalyzed by Samples Containing Well Defined Ensembles of Vanadium

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Samples containing either vanadium oxide or heteropolyanions having the Keggin structure, $[PW_{12-n}V_nO_{40}]^{(3+n)-}$ or $[SiW_{12-n}V_nO_{40}]^{(4+n)-}$ $\{n = 0, 1, 2, 3\}$, or a modified Keggin structure, $[PV_{14}O_{42}]^{9-}$, each supported on silica at nearly 100% fraction exposed, were employed to determine the minimum number of adjacent vanadium ions required to catalyze the oxidative dehydrogenation of methanol to make formaldehyde. When the reaction was run under conditions of low, differential conversion (where the structures of the substituted Keggin ions were shown to remain largely intact), the turnover frequency per vanadium for the production of formaldehyde increased by less than a factor of 2 as the size of the exposed vanadium ensembles increased from V_1 to V_3. Thus, the reaction appears to be independent of the adjacency of vanadium ions. The rate of the principal competing reaction, dehydration of methanol to make dimethyl ether, was found to depend sensitively on surface charge density: it decreased exponentially as the anion charge was made more negative either by replacing P with Si or by replacing W with V. The latter substitution provided a way to prepare catalysts whose activity *and* selectivity could be increased together.

INTRODUCTION

There is disagreement in the literature on the oxidative dehydrogenation of methanol concerning the extent to which the rate of production of formaldehyde depends on the surface structure of the transition metal oxides employed as catalysts. The first reports that the reaction network of methanol oxidation could be called structure sensitive (*1–7*) were based on patterns of activity and selectivity that varied with the morphology of bulk crystals of molybdena and vanadia. More recently, however, Gasser and Baiker (*8*) found that areal activity for the production of formaldehyde depended only weakly on the sort of structural differences that they could produce by employing various crystalline and amorphous samples of vanadium pentoxide as catalysts. Disagreements also occur when surface loading has been employed to vary surface structures. Louis *et al.* (*9*) and Niwa *et al.* (*10*) have suggested that oligomerization of Mo–O units on the surface of silica or tin oxide strongly affects N_f, the rate of production of formaldehyde per surface metal ion. On the contrary, Kim *et al.* (*11*) present data showing that N_f varies by less than a factor of 2 across a series of silica-supported chromia catalysts in which the chromium loading increased 15-fold and the initial surface species of chromium oxide under hydrated conditions, as determined by Raman spectroscopy, changed from a mixture of monomers, dimers, and trimers to predominately trimers and then tetramers. They attribute the constancy of N_f to the evolution of all the precursors into isolated mononuclear chromia species under reaction conditions.

To learn more about the sensitivity of the oxidative dehydrogenation of methanol to the structure of the catalyst, we have attempted to probe the effect of next nearest neighbors in the oxide lattice. Our approach employed catalysts prepared from a

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series of silica-supported heteropolyanions, $[PW_{12-n}V_nO_{40}]^{(3+n)-}$ $\{n = 0, 1, 2, 3\}$, in which the vanadium ions could be made to occupy adjacent sites in the Keggin framework (Fig. 1). In addition, the use of catalysts prepared from the more negatively charged silicon analogs, $[SiW_{12}O_{40}]^{4-}$ and $[SiW_{11}VO_{40}]^{5-}$, provided means to study the influence of surface charge density on the selectivity of the catalysts.

EXPERIMENTAL

Preparation of the Heteropolyanions

Procedures for preparing the heteropolyanions used in this study were adapted from literature recipes (*12–16*). The parent Keggin ions, $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$, were prepared as the acids by direct precipitation from solutions containing the sodium salts of WO_4^{2-} and either HPO_4^{2-} or SiO_3^{2-}. The monolacunary compound, α-$K_7PW_{11}O_{39}$, was prepared by careful hydrolysis of the parent tungsten ion using potassium bicarbonate. The trilacunary compound, β-$Na_8HPW_9O_{34}$, was prepared by careful addition of acetic acid to a solution of phosphoric acid and sodium tungstate. The monosubstituted anions, $[PW_{11}VO_{40}]^{4-}$ and $[SiW_{11}VO_{40}]^{5-}$, were prepared as potassium salts from the parent, all-tungsten ions by careful hydrolysis with lithium or sodium carbonate followed by addition of a solution containing the VO_3^- ion and then precipitation using potassium chloride. Potassium salts of the di- and trisubstituted anions, α-1,2-$[PW_{10}V_2O_{40}]^{5-}$ and α-1,2,3-$[PW_9V_3O_{40}]^{6-}$, were synthesized by adding vanadium ions to a solution containing the trilacunary compound. An isomerically impure disubstituted Keggin anion, in which the vanadium ions had been deliberately scrambled intramolecularly, was prepared by prolonged refluxing of a solution of PV2. An all-vanadium heteropolyanion, $K_9PV_{14}O_{42}$, was prepared by adding phosphoric acid to a solution containing sodium vanadate followed by precipitation with potassium chloride. Acids were converted to sodium salts by the neutralization with a stoichiometric quantity of sodium carbonate. Potassium salts were converted to sodium salts by exhaustive elution through an Amberlite IR120 exchange resin previously loaded with sodium ions by washing with sodium chloride according to the manufacturer's instructions (*17*). We note that we did not perform elemental analyses to confirm the completeness of either method of introducing the sodium ions, relying instead on a presumed efficacy of the treatments: acid-base neutralizations and ion-exchanges with large excesses of the incoming cation (Na : K = 80 : 1).

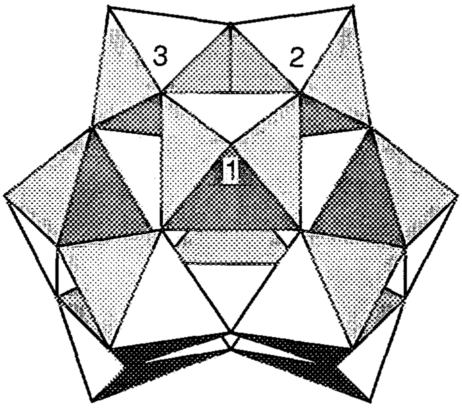

FIG. 1. Location of the substitution positions in the Keggin structure.

The structures and isomeric purity of the starting heteropolyanions were confirmed by infrared spectroscopy (Nicolet, 7199 FT-IR system) and, where possible, by ^{31}P NMR spectroscopy (Bruker Wm-250 FT spectrometer) in order to rule out the presence of degradation products or positional isomers. The infrared spectra of KBr disks containing the bulk compounds (Fig. 2) showed only the expected bands (*18*) at ca. 810 and 887 cm^{-1} (W–O–W stretches), at 990 cm^{-1} (W=O stretch), and 1100 cm^{-1}. The latter band corresponds to a triply degenerate set of vibrations of the phosphate group buried in the core of the Keggin structure (*18*). This band tracked the progressive substitution of W by V splitting

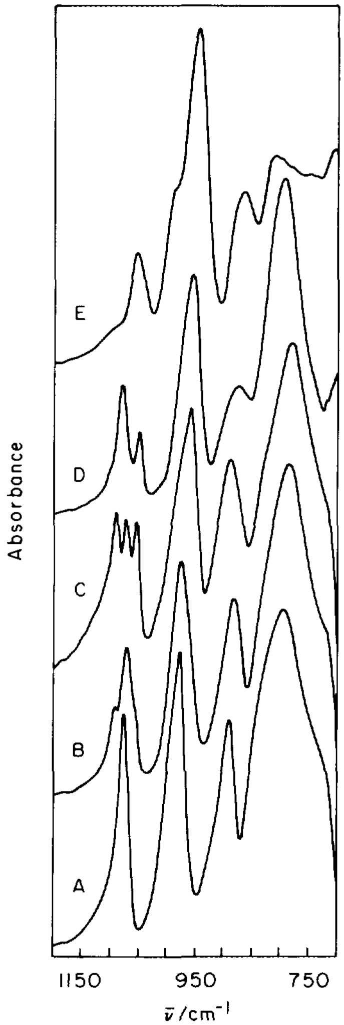

FIG. 2. Infrared spectra of the bulk compounds used as starting materials. (A) $K_3PW_{12}O_{40}$; (B) $K_4PW_{11}VO_{40}$; (C) α-1,2-$K_5PW_{10}V_2O_{40}$; (D) α-1,2,3-$K_6PW_9V_3O_{40}$; and (E) $K_9PV_{14}O_{42}$.

into three and then melding back into two peaks as the point group of the cluster changed from T_d (parent compound) to C_s (disubstituted) to C_{3v} (trisubstituted). The monosubstituted cluster, $[PW_{11}VO_{40}]^{4-}$, also belongs to the point group C_s, but apparently the substitution breaks the symmetry around the phosphorus only to the extent of creating shoulders on the main peak at 1100 cm^{-1}.

For the NMR measurements, samples were dissolved in water at the concentration and pH that were used in the impregnation step (0.09 M, pH 1.5–4.9). As an additional check on isomeric purity, the spectra of the mono-, di-, and trisubstituted phosphate anions were also measured at pH 2 (adjusted with HNO_3) to ensure a proper comparison with literature spectra of the highly pH-dependent chemical shifts. All spectra were recorded with the samples held in coaxial tubes that contained D_2O in the outer shell to lock the field frequency. Peak positions (Tables 1 and 2) were referenced to an external sample of phosphoric acid. With two exceptions, a single, sharp resonance was observed for all the solutions indicating that only one isomer of the heteropolyanions was present. Moreover, as shown in Table 2, the resonances matched those reported for authentic samples. The exceptions were the PV2 precursor and the deliberately scrambled sample prepared from it. The spectrum of PV2 contained two peaks, one at −13.6 ppm and the other at −12.8 ppm, with relative peak areas of 95 : 5. The dominant peak lay at the position expected for this anion (*13*); the smaller peak could result from an additional di-substituted isomer or perhaps another vanadium-substituted cluster. Given its low concentration, however, we have ignored the impurity in the discussion of the results. As expected, the ^{31}P NMR spectrum of a solution of the isomerically impure, disubstituted Keggin ion, PV2(scrambled), contained five peaks in the 1 : 2 : 2 : 2 : 4 intensity ratios that corresponded to a statistical distribution of the disubstituted isomers (*19*).

Preparation of Supported Catalysts

The characteristics of the supported samples and the abbreviations employed to designate them are given in Table 1. Silica was chosen as the support material since previous work (*20–22*) had shown that heteropolyanions deposited on it were more resistant to thermal degradation than were

TABLE 1

Current Samples

Sample	Symbol	^{31}P NMR peak *position/ppm* of impregnating solution	pH of *impregnating* solution	Loading V (*wt%*)	Surface area (m^2 g^{-1})
Silica (lot 1C031)	—	—	—	0.00	230
Silica (lot 1H074)	—	—	—	0.00	196
$Na_7PW_{11}O_{39}/SiO_2$	PW11	−10.9	3.7	0.00	Not measured
$Na_3PW_{12}O_{40}/SiO_2$	PW	−14.5	1.5	0.00	169
$Na_4SiW_{12}O_{40}/SiO_2$	SiW	—	1.5	0.00	160
$Na_4PW_{11}VO_{40}/SiO_2$	PV	−13.9	3.1	0.27	163
$Na_5SiW_{11}VO_{40}/SiO_2$	SiV	—	3.1	0.27	158
$Na_5PW_{10}V_2O_{40}/SiO_2$	PV2	−13.6, −12.8 (95 : 5)	3.5	0.56	166
$Na_5PW_{10}V_2O_{40}/SiO_2$	PV2 (scrambled)	−10.1, −12.7, −12.9, −13.4, −13.6 (1 : 2 : 2 : 2 : 4)	Not measured	0.56	166
$NaVO_3$ + Na_3PO_4 + $(NH_4)_6H_2W_{12}O_{40}$ supported on silica Na : P : W : V = 5 : 1 : 10 : 2	P+W+V2	Several lines between −5 and −15 ppm			
$Na_6PW_9V_3O_{40}/SiO_2$	PV3	−12.7	4.9	0.88	158
$Na_7PV_{14}O_{42}/SiO_2$	PV14	+1.0	1.8	4.08	139
Vanadia/SiO_2	—	Not measured	4.0	0.30	—

those deposited on other, high surface area carriers (Al_2O_3, TiO_2, ZrO_2). A commercially available fumed silica (Cab-O-Sil, M5, 230 or 196 m^2/g surface area by N_2 BET, wet point of 0.7 cm^3/g) was impregnated by the incipient wetness technique with water solutions of the sodium salts of the heteropolyanions. Typically, 2 g of silica, previously dried in air at 393 K were placed in a ceramic bowl and 1.4 cm^3 of impregnating solution (0.09 mol/liter) was added dropwise with constant mixing over 30 min. The concentration of salt was such that about 15 area% of the silica would have been covered by the Keggin anions (1.1 nm diameter) if the anions had spread uniformly across the surface of the support. This corresponded to a mass loading of approximately 15 wt%. The supported samples were dried overnight in air at 393 K and the resulting powders were pressed into wafers (8000 psig, i.e., 55 MPa), then crushed and sieved to give 0.3 to 0.6 mm particles which were again dried in air at 393 K prior to use in the reaction rate measurements.

TABLE 2

Comparison of ^{31}P NMR Chemical Shifts of the Catalyst Precursors with Literature Values

Anion	This work[a] (ppm)	Literature[b] (ppm)
$[PW_{11}VO_{40}]^{4-}$	−14.18	−14.19
1,2-$[PW_{10}V_2O_{40}]^{5-}$	−13.56	−13.61
1,2,3-$[PW_9V_3O_{40}]^{6-}$	−13.42	−13.41

[a] pH 2, 0.1 *M* solutions, Na^+ counterions.

[b] After Domaille (*13*).

The sample called Vanadia/SiO_2 was also prepared by incipient wetness using an 0.08 *M* solution of NH_4VO_3 adjusted to pH 4 with nitric acid. According to the literature

(*23*), at this pH, the predominant vanadium species in solution is the isopolyanion, $V_{10}O_{27}(OH)^{5-}$. The supported sample was dried overnight in air at 383 K and then calcined in air at 673 K for 2 h to remove the ammonia.

Another impregnated sample, called P+W+V2, was prepared using an aqueous solution of Na_3PO_4, $(NH_4)_6H_2W_{12}O_{40}$, and $NaVO_3$ so as to give the same amounts of P, W, and V as were deposited using $Na_5PW_{10}V_2O_{40}$ but without necessarily producing the structure of the disubstituted heteropolyanion. Correspondingly, the ^{31}P NMR spectrum of the impregnating solution contained several lines of low intensity, having chemical shifts between −5 and −15 ppm, which indicated the presence of several heteropolyanions and fragments. In particular the simple tungstate anion, WO_4^{2-}, and the vanadium iospolyanions, $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$, may have been present since the solution was slightly basic (pH = 7.6).

Characterization of Catalyst Samples

Composition of the samples was determined before and after use in the reaction rate measurements by means of X-ray fluorescence spectroscopy (Phillips XRD), infrared spectroscopy (Nicolet 7199), X-ray diffraction (Phillips AXS), and transmission electron microscopy (Phillips EM400T, 100kV, bright field images).

Reaction Rate Measurements

The reactor consisted of a Pyrex tube (1 cm inside diameter) equipped with a sintered glass disk for supporting the catalyst samples and a sand bath for distributing the heat supplied by a clamshell tube furnace. Temperature was measured with a stainless steel-jacketed thermocouple (type K) that could be positioned at different heights along the axis of the reactor to check for hot spots. Mass flow controllers (Brooks 5850) were employed to meter the helium (Airco, 99.995%) and dioxygen (Airco, 99.6%, the major impurities being argon and dinitrogen). Methanol (Fischer Spectranalyzed Grade) was vaporized in a constant temperature bubbler operating at 273 K. The concentration of methanol in the feed was controlled by varying the split ratio of a portion of the oxygen and helium feed. The standard concentrations in the feed stream were 3 mol% for methanol and 5 mol% for dioxygen. Total gas flow rates ranged from 0.58 to 6.67 cm^3/s (STP). Transfer lines before the reactor were heated to 393 K to prevent condensation of the methanol; exit lines were heated to 423 K to prevent polymerization of formaldehyde. The feed and exit streams were analyzed by gas chromatography (Hewlett–Packard 5880) using a system of multiport gas sampling valves controlled by a computer onboard the GC. Carbon dioxide, formaldehyde, dimethyl ether, water, methanol, methyl formate, dimethoxymethane, and dioxygen plus carbon monoxide were analyzed by thermal conductivity detection after passage through a temperature programmed, 2-m column of 60/80 mesh Porapak T. The amount of carbon monoxide alone was determined by use of a second column (2 m of 120/140 Carbosieve S) followed by a methanizer and a flame ionization detector. Mass balances for carbon and oxygen could be closed to better than 5% by correcting the measured concentrations for the small pressure drop through the reactor.

Catalyst samples, 0.5 g, were pretreated in the reactor by increasing the temperature linearly at 5 K/min to 625 K under a flow of 100 cm^3/min of 25% O_2. The temperature was then held at 625 K for 1 h before the flow of methanol was started. A 1–2 K rise in the temperature of the bed accompanied the introduction of the methanol. Operating parameters were selected in no fixed pattern. The reactor was operated continuously for runs lasting from 4 to 6 days. Hysteresis with respect to temperature was checked for but not found. The existence of intraparticle concentration gradients, gas by-passing, and axial diffusion were ruled out by experiments in which the mesh size of the catalyst particles and the height of the catalyst bed were varied.

RESULTS

Existence and Persistence of Keggin Structures

We did not measure elemental analyses of either the starting compounds or the supported samples since such assays could not assist us in determining the isomeric purity of these materials. Nor could elemental analyses alone rule out the possibilities of decomposition or disproportionation of the clusters. Instead, we have relied on the NMR spectra of the starting materials and the excellent agreement of their NMR and IR spectra with those contained in the literature to establish the identity of the major, and likely only, species present in the impregnating solutions. Subsequently, we inferred from the constancy of the infrared spectra that the chosen isomers of the heteropolyanions were initially present on the surface of the silica support and that the structures survived intact during reaction. For example, supported PV3 exhibited IR bands in the same positions as those of the bulk salt (Table 3). While the intensities and positions of these bands changed slightly after the sample had been used as a catalyst for 6 days (Fig. 3), the spectrum contained no new bands that would accompany the development of decomposition products. Eguchi *et al.* (*24*) observed comparable and reversible decreases in infrared spectra of $[PMo_{12}O_{40}]^{3-}$ that had been reduced with dihydrogen. Thus, the spectral changes we observed may have been due merely to differences in the extent of reduction of the before and after samples at the time when their IR spectra were measured. Similar results were found for the PW12, PV, PV2, SiW12, and SiV samples (Table 4). In all cases, strong and readily identifiable bands characteristic of the Keggin structures were observed in the spectra of the samples before and after reaction. Typically, about 95% of the band intensities persisted with the largest decreases occurring in the ν_3 and ν_4 bands (bridging M–O–M vibrations).

TABLE 3

Comparison of IR Band Positions in Bulk and Supported $[PW_9V_3O_{40}]^{6}$

Sample	ν_1 (cm^{-1}) (*P–O*)	ν_2 (cm^{-1}) (*M=O*)	ν_3 (cm^{-1}) (*M–O–M*)	ν_4 (cm^{-1}) (*M–O–M*)
Bulk $K_6PW_9V_3O_{40}$	1085 1055	962	877	797
Supported PV3 (before reaction)	1082 1071 1052	960	882	814

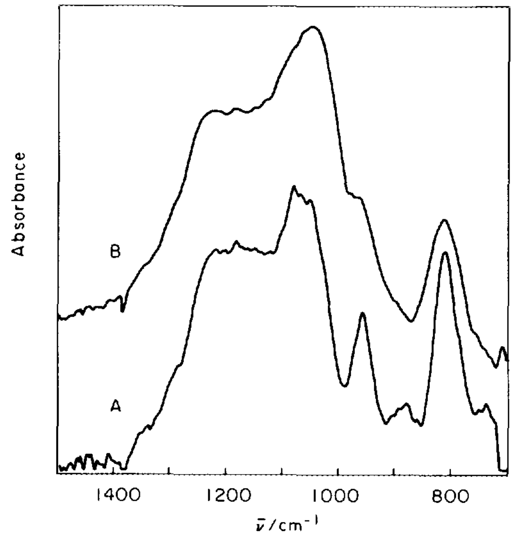

FIG. 3. Comparison of IR spectra of PV3 before (A) and after (B) use.

There were, however, significant differences between the spectra of the supported PV14 sample (Fig. 4) and its bulk salt (Fig. 2e). For instance, bands observed at 1229 and 1160 cm^{-1} in the spectra of the supported sample were not present in the spectrum of the bulk compound. In addition, the bulk heteropolyanion displayed a sharp band at 868 cm^{-1} which was missing in the spectra of the supported samples. From these differences we concluded that the PV14 structure decomposed to form a new oxide on the support. The new structure appeared to be stable, however, since the

TABLE 4

Comparison of IR Band Positions and Intensities for Supported Phosphate Samples before and after Use in the Conversion of Methanol

Sample	Condition	ν_1 (cm^{-1}) (P–)	ν_2 (cm^{-1}) (M=O)	ν_3 (cm^{-1}) (M–O–M)	ν_4 (cm^{-1}) (M–O–M)
PW12	Fresh	1070s	983m	892s	809s
	Used	1070s	983sh	892s	811s
PV	Fresh	1068s	980s	880s	823s 811s
	Used	1066s	980m 961sh	897m 884m	823s 814s
PV2	Fresh	1049s 1066s	964s	895s	814s
	Used	1043s	966sh	895sh	812s
PV3	Fresh	1082s 1071s 1052s	960s	882m	814s
	Used	1047s	980sh 964sh	899sh	811s
PV14	Fresh	1229s 1159m 1049s	962m	824m	806m
	Used	1237s 1160m 1049s	958m	824w	806w

Note. Band intensities are indicated as sharp (s), medium (m), weak (w), or shoulder (sh).

spectra of the samples before and after they converted methanol were almost identical.

X-ray fluorescence spectroscopy, which were determined only for the samples in the PV*n* series, showed no significant changes after reaction in the contents of tungsten, vanadium, or phosphorus (Table 5).

Transmission electron micrographs of all the supported heteropolyanion samples except PV14 showed uniform 3–4 nm particles evenly distributed on the 14–16 nm particles of the silica support (Fig. 5). The smaller particles were still apparent after

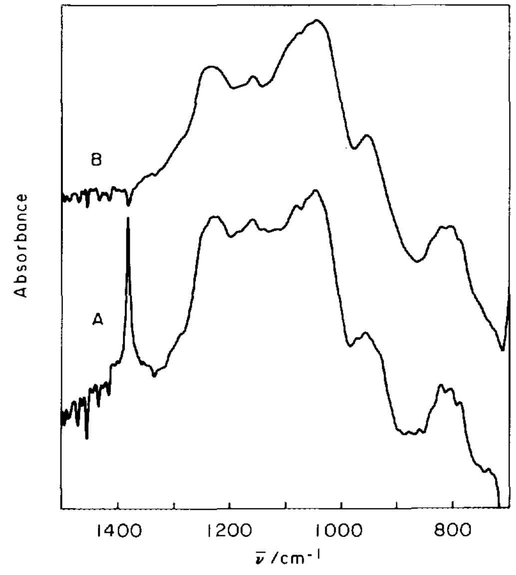

FIG. 4. Comparison of IR spectra of PV14 before (A) and after (B) use. The spike is most likely due to nitrate ions that decompose when the sample is heated.

TABLE 5

Composition of Samples as Determined from X-ray Fluorescence before and after Use

Sample	Condition	Peak intensity[a]		
		W	V	P
PW12	Fresh	5.5	—	4.0
	Used	5.4	—	4.0
PV	Fresh	5.2	1.3	4.0
	Used	5.3	1.3	4.0
PV2	Fresh	5.0	1.7	3.8
	Used	5.1	1.7	3.8
PV3	Fresh	4.9	2.2	4.0
	Used	5.1	2.1	4.0

[a] Signals were not compensated for matrix effects but were measured at the same areal loading before and after reaction. Thus, only W–W, V–V, and P–P comparisons are valid.

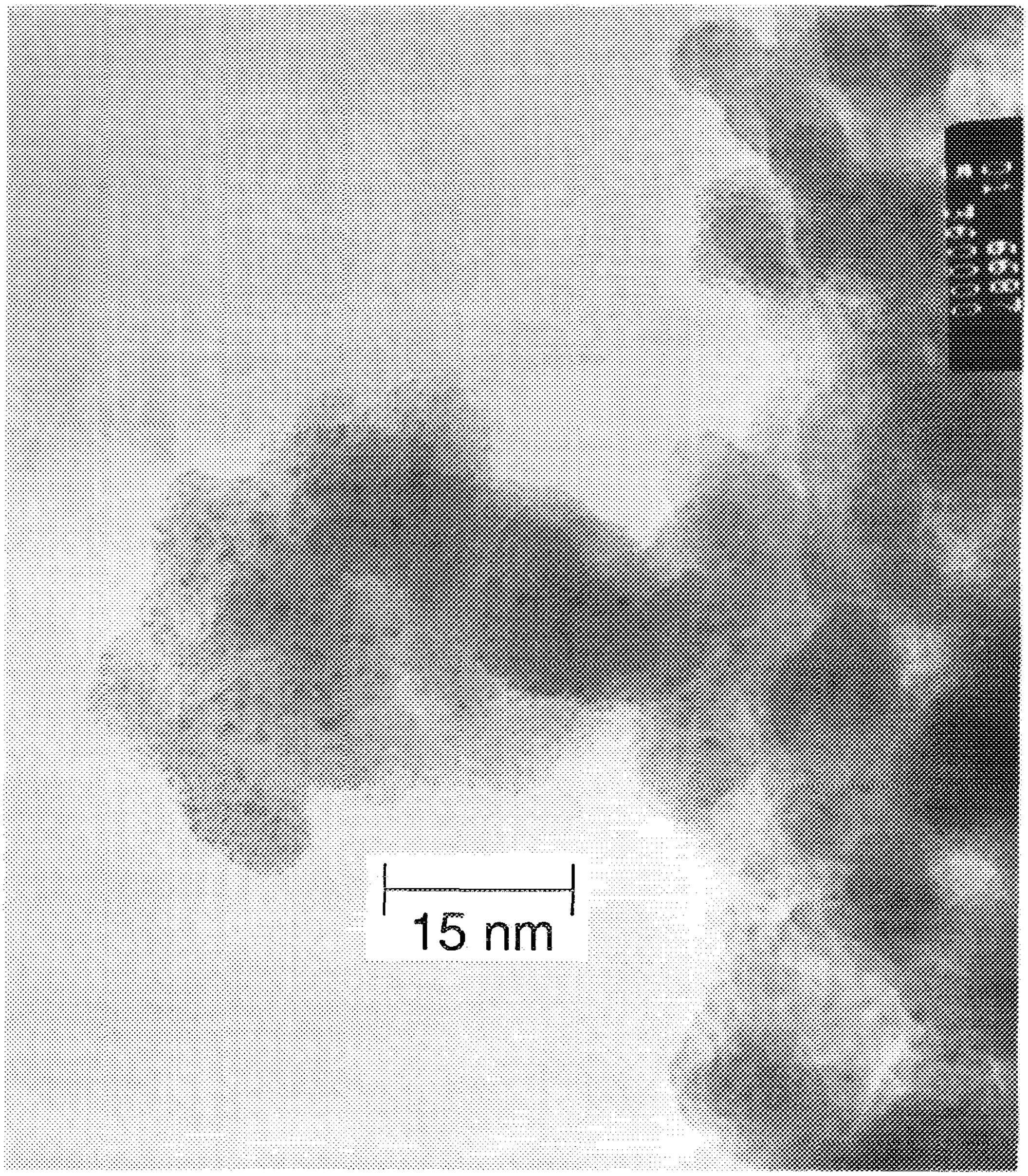

FIG. 5. Electron micrograph of PV3 before use.

reaction. Likewise, X-ray powder patterns of all the supported heteropolyanion samples except PV14 contained a persistent feature at an angle of $2\theta = 8.7°$ (Fig. 6) that could be assigned to diffraction from either the (110) or (111) plane of the cubic lattice common to all the heteropolyanion salts. From the Debye–Scherrer equation, the widths of the peaks were calculated to correspond to coherence lengths of about 3 nm, in good agreement with the results from the microscopy. A cubic agglomerate of this size would have only 2–3 heteropolyanions along a side, all of which would

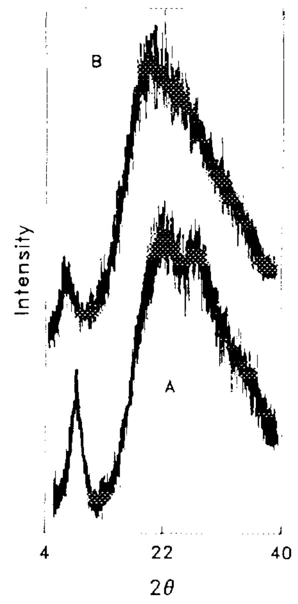

FIG. 6. Comparison of X-ray powder patterns of PV3 before (A) and after (B) use.

be accessible to incoming reactants. The PV14 sample exhibited neither the small particles in its micrograph nor the low angle feature in its diffractogram, consistent with the decomposition of the original anion also inferred from the IR results.

Overall Activity

The reactor came to a steady state within 30 min under all conditions and could be maintained in that state for at least 3 days. Axial temperatures through the catalyst bed varied less than 1 K when the overall conversion of methanol was maintained at or below 10%; hot spots (1–5 K) developed when the conversion exceeded 20%. The empty reactor contributed less than 1% of the conversion of methanol under the most severe conditions employed during the kinetics measurements (3% methanol, 25% dioxygen, total flow rate of 0.58 cm^3/s, 625 K).

Methanol conversion (Fig. 7) increased with increasing molar contact time (moles of heteropolyanion in sample divided by the molar flow rate of methanol in the feed). Methanol conversion by the vanadium-containing samples increased with vanadium content. The parent pertungsten samples displayed intermediate activity; the lacunary ion, PW11, was the least active sample.

As has been noted by others (*25, 26*), the fumed silica we used for a support is itself a catalyst for the oxidation of methanol. Under the conditions we employed, however,

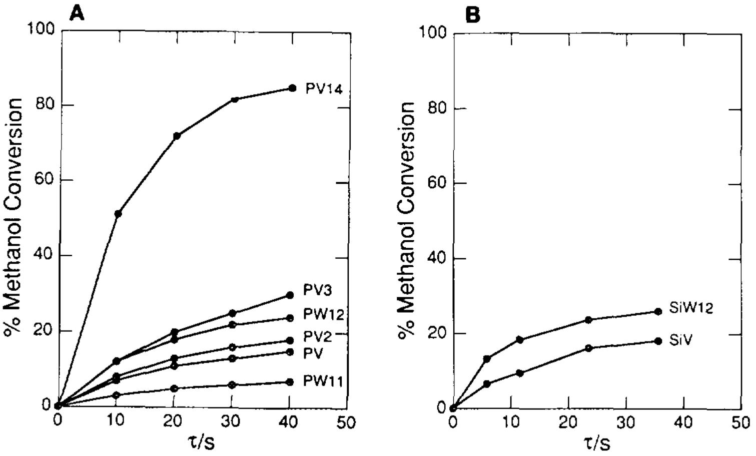

FIG. 7. Conversion of Methanol catalyzed by supported heteropolyanions. (A) PV*n* series and (B) SiV*n* series. The contact time, τ, equals the amount of Keggin ion in the reactor (mol) divided by the flow rate of methanol (mol/s).

TABLE 6

Methanol Conversion Catalyzed by the Silica Support at 625 K, 3% CH_3OH, 25% O_2

Sample	Reaction rates at 10% total conversion (μmol g^{-1} s^{-1})				
	CH_3OH	CH_2O	CO_2	CO	HCOOH
SiO_2	−6.73	0.78	0.50	0.21	5.24
SiO_2 impreg. with 2.1 wt% NaCl	−0.68	0.27	0.34	0.07	0.00

it gave a product slate that included formic acid and methyl formate (Table 6), neither of which was observed in significant quantities among the products of the PV*n* samples. The activity peculiar to the silica, as measured by the production of methyl formate, could be suppressed by adding sodium to the silica (*25*) or by decreasing the partial pressure of dioxygen to 5% (Fig. 8). Since the heteropolyanion catalysts were all prepared from sodium salts, and since the rate measurements reported below were, for the most part, measured at 5% concentrations of dioxygen, we have not corrected the activity data for any contribution from the support.

Selectivity Patterns

Formaldehyde, dimethyl ether, methyl formate, carbon monoxide, carbon dioxide, dimethoxymethane, and water (not shown) were the only products that could be detected when the reactor contained the heteropolyanion-impregnated silica (Figs. 9 and 10). Selectivities depended on conversion but not very strongly, tending as would be expected toward the more oxidized products at higher contact times. The least active sample, PW11, was also the least selective catalyst (Fig. 9a). The other, all-tungsten compounds, PW12 and SiW12, displayed high selectivity to dimethyl ether (Figs. 9b, 10a), consistent with their known activity as acid catalysts (*27–35*).

For the phosphorus-series of catalysts, two products, formaldehyde and dimethyl ether, accounted for 90+% of the carbon balance. The production of formaldehyde increased montonically—and that of dimethyl ether decreased—with the introduction of vanadium ions in the Keggin framework (Figs. 9c–9f). These trends are

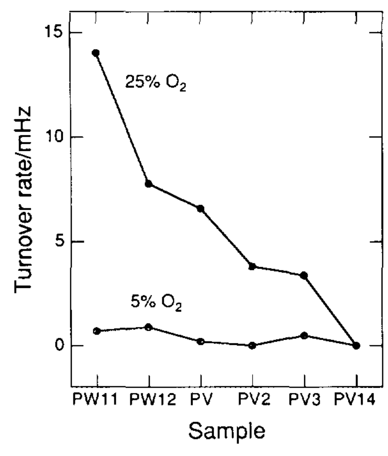

FIG. 8. The residual catalytic activity of the support as estimated by the formation of methyl formate. Conditions: 3 mol% CH_3OH, 5 or 25 mol% O_2; 625 K. The reaction rates are normalized by the amount of Keggin ion used to prepared the catalysts.

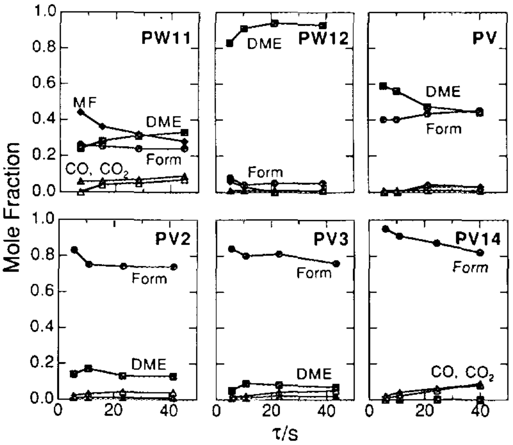

FIG. 9. Products of methanol conversion catalyzed by supported PV*n* heteropolyanions. Conditions: 3 mol% CH_3OH; 5 mol% O_2, 625 K (●, formaldehyde; ■, dimethyl ether; ▲, CO_2; △, CO; ◆, methyl formate).

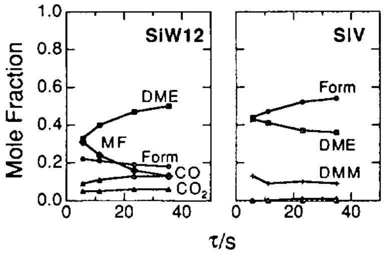

FIG. 10. Products of methanol conversion catalyzed by supported SiV*n* heteropolyanions. Conditions: 3 mol% CH$_3$OH; 5 mol% O$_2$, 625 K (●, formaldehyde; ■, dimethyl ether; ▲, CO$_2$; △, CO; ◆, methyl formate; ×, dimethoxymethane).

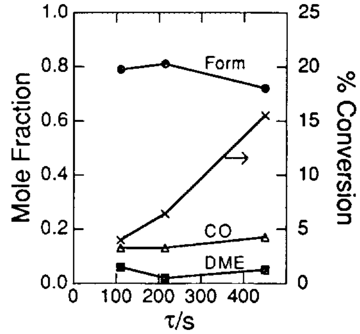

FIG. 12. Products of methanol conversion catalyzed by Vanadia/SiO$_2$. Conditions: 3 mol% CH$_3$OH; 5 mol% O$_2$, 625 K (●, formaldehyde; ▲, CO$_2$; △, CO).

evident in Fig. 11, which compares the selectivity for the principal products at a common level of methanol conversion (chosen to be 10% in order to ensure thermal and compositional homogeneity in the reactor). The two silico-heteropolyanions behaved like their phosphorus analogs except that the former also produced moderate quantities of methyl formate and dimethoxymethane even when the concentration of dioxygen was kept as low as 5% (Fig. 10).

Supported vanadium oxide was selective for the production of formaldehyde (Fig. 12), much like the all-vanadium heteropolyanion, PV14 (Fig. 9f). Finally, P+W+V2, the sample prepared to have the same composition as the Keggin ion PV2, was notably less selective for the production of formaldehyde (Fig. 13) than was the catalyst prepared from the actual heteropolyanion.

Turnover Rates

For convenience in comparing the activity of all of the samples of heteropolyanion, the rates for the production of formaldehyde and dimethyl ether were normalized

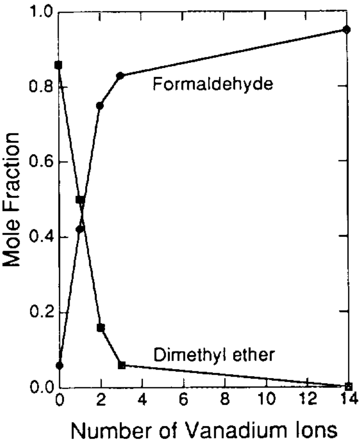

FIG. 11. Summary of the principal products of methanol conversion (10%) catalyzed by supported PV*n* heteropolyanions. The points were calculated by linear interpolation from the data shown in Figs. 7 and 9. (●, formaldehyde; ■, dimethyl ether).

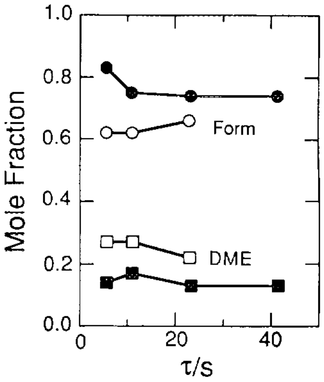

FIG. 13. Comparison of the selectivities of catalysts prepared from PV2 (solid) and from a solution containing the same elemental composition (open). Conditions: 3 mol% CH$_3$OH; 5 mol% O$_2$, 625 K (● and ○, formaldehyde; ■ and □, dimethyl ether).

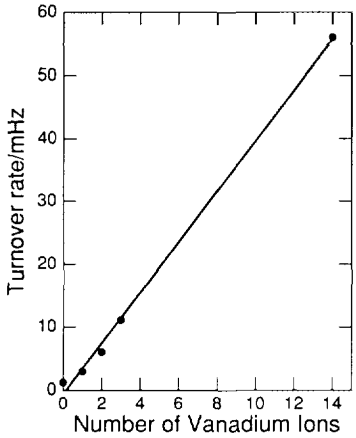

FIG. 14. Rate of production of formaldehyde normalized by the quantity of heteropolyanion in the catalysts. Conditions: 625 K; 3 mol% CH_3OH; 5 mol% O_2; 625 K.

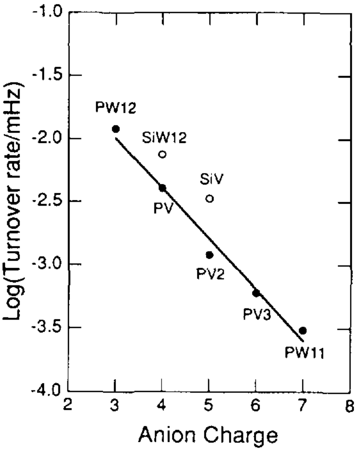

FIG. 15. Rate of production of dimethylether normalized by the quantity of heteropolyanion in the catalysts. Conditions: 625 K; 3 mol% CH_3OH; 5 mol% O_2; 625 K.

by the amount of Keggin ion used in the preparation of the catalysts placed in the reactor. The resulting turnover frequency for formaldehyde, N_f, was strikingly linearly dependent on the number of vanadium ions in the heteropolyanions (Fig. 14). Indeed, Table 7 shows that the reaction rate normalized by number of vanadium ions, N_f/V, was remarkably constant across wide variations in preparation and composition of the catalysts. The turnover rate per Keggin ion for the production of dimethyl ether, N_e, was a decreasing function of the number of vanadium ions in the Keggin and, more generally, of the overall negative charge on the anions (Fig. 15).

Arrhenius plots for the production of formaldehyde were constructed for the catalysts in PV*n* series (Fig. 16). The catalysts

TABLE 7

Rates of Production of Formaldehyde Normalized by Vanadium Content of the Catalysts[a]

Sample	Turnover rate (mHz)	V loading (wt%)
PV	2.9	0.27
SiV	3.3	0.27
PV2	3.0	0.56
PV2 (scrambled)	3.2	0.56
P+W+V2	3.3	0.56
PV3	3.7	0.88
PV14	4.0	4.08
Vanadia/SiO_2	4.3	0.30
V_2O_5/SiO_2[b]	4.3	0.56

[a] Rates measured at 625 K, 3% CH_3OH, 25% O_2, 10% total conversion.

[b] Extrapolated from the results of Deo and Wachs (*47*) using an activation energy of 80 kJ/mol and the rate expression proportional to $P_{CH_3OH}^{0.74}P_{O_2}^{0.22}$.

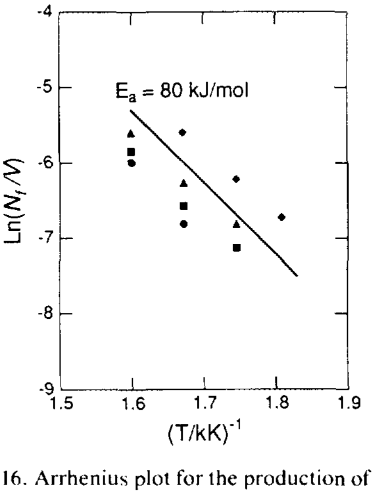

FIG. 16. Arrhenius plot for the production of formaldehyde. Rates are normalized by the amount of surface vanadium in the samples. Conditions: 3 mol% CH_3OH; 5 mol% O_2.

TABLE 8

Exponents in the Power Law Rate Expressions, $r = kP^{m}_{CH_3OH}P^{n}_{O_2}$ for the Production of Formaldehyde and Dimethylether at 10% Conversion of Methanol: P_{CH_3OH} = 0.6 to 4.2 kPa; P_{O_2} = 4.5 to 28 kPa

Sample and reaction	*m*	*n*
PV, CH_2O	0.94	0.32
PV14, CH_2O	0.73	0.22
Molybdenum oxides, CH_2O[a]	0.3–0.9	0.1–0.3
PV, CH_3OCH_3	0.84	−0.32

[a] From Machiels and Sleight (*37*).

shared the same activation energy, 80 kJ/mol, a value close to that found in the literature for the oxidative dehydrogenation of methanol (*8, 36–42*). In addition, as would be expected from the linearity of the plot in Fig. 14, the heteropolyanion catalysts shared nearly the same preexponential factor when the reaction rates were normalized by the amounts of vanadium in the samples. Rate equations for both of the principal products could be expressed in the form of power laws where the exponents had values comparable to those found in the literature (Table 8). The exponents should not be given too much significance because they also reflect the participation of the support at higher concentrations of dioxygen.

DISCUSSION

The large changes in selectivity summarized in Fig. 11 confirm the conventional expectation that the conversion of methanol involves reactions whose rates depend strongly on the structures exposed on the surface of an oxide catalyst. However, the data presented in Fig. 14 and Table 7 show that N_f/V is nearly independent of the adjacency of the vanadium ions in the catalysts. (Regrettably, the middle portion of Fig. 14 cannot be filled in at this time since, to our knowledge, syntheses resulting in isomerically pure Keggin ions containing 4 through 11 vanadium ions have not yet been devised.) If it were the case that an ensemble containing more than a single vanadium ion was needed to catalyze the oxidative dehydrogenation of methanol then both the curve plotted in Fig. 14 and the tabulated results would depend in a more complicated way on the vanadium content of the catalysts. We note that the catalysts were prepared from materials that likely have quite different thermal stabilities yet displayed nearly identical turnover rates per vanadium ion that were stable for days across the 50-K excursions in temperature needed to construct the Arrhenius plots. We therefore discount the possibility that all of the samples decomposed according to their vanadium loadings to yield exactly the same proportion of some other, very active phase. Instead, we propose that the oxidative dehydrogenation of methanol only involves a single vanadium center, at least under the conditions we employed where reoxidation of the catalyst is not a kinetically significant step. (When reoxidation is kinetically significant, as it appears to be in the liquid phase oxidative dehydrogenation of terpinene catalyzed by $H_6PMo_{10}V_2O_{40}$ (*43*), then the reaction rate does depend strongly on the local concentration of vanadium ions.)

Figure 15 shows that N_e, the rate of the dehydration reaction per Keggin ion depends exponentially on the overall charge of the anion employed to prepare the sample. These results can be accommodated by a simple, electrostatic model of the acidity of the Keggin ions. First, assume that the supported samples comprise a family of acids whose catalytic activity can be correlated through a Brønsted relation,

$$k = cK^{\alpha}, \tag{1}$$

where k is the rate constant and K is the acid dissociation constant for a particular anion, A:

$$K = e^{-\Delta G/RT} = e^{-(\Delta H - T\Delta S)/RT}. \tag{2}$$

In the simple model depicted in Fig. 17, an electrostatic contribution to the strength of the acid HA arises from the Coulombic attraction between the negatively charged

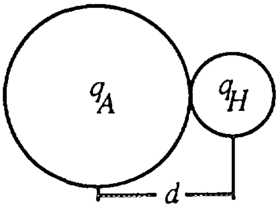

FIG. 17. Electrostatic model of the Brønsted acidity of the supported heteropolyanions.

Keggin ion (q_A) and the positively proton (q_H). The energy of this interaction can be expressed as a term in the enthalpy of dissociation:

$$\Delta H = \Delta H_0 + \frac{q_A q_H}{4\pi\varepsilon_0 d}. \tag{3}$$

It is reasonable to assume that ΔH_0, ΔS, q_H, and d, like α and c, are the same for all the Keggin ions since their molecular structures are so similar. Thus, after a straightforward algebraic manipulation of Eqs. (1)–(3) and the introduction of a new constant, μ ($= \alpha\ q_H/4\pi\varepsilon_0 d$), the rate constant of a particular catalyst relative to one chosen as a standard (k_0) is found to depend exponentially on the difference in charge between the supported anions, $\Delta q = (q_A - q_0)$:

$$k = k_0 e^{(\mu\Delta q/RT)}. \tag{4}$$

The value of μ determined from the slope of the line in Fig. 15 is 51 mV, which is about 50 times smaller than we calculate by assuming $\alpha = 0.5$, $q_H = +1$, and $d = 0.6$ nm (sum of the radii of H^+ and the Keggin anion). The agreement is satisfactory given that our model ignores any influence of the electric field provided by the sodium cations, whose number necessarily increased with charge on the anions and which have also been found to affect the acidity of Keggin ions (*27*, *30*, *35*, *44*). Our model also does not account for differences in the average oxidation state of the Keggin ions in the various catalysts. However, given the rather weak dependence of the rate of production of dimethyl ether on overall conversion and on oxygen pressure, it is unlikely that any of the catalysts were substantially reduced under the reaction conditions we employed.

Despite its simplicity, this model generates a correlation that fits the data over a thirty-fold variation in turnover rates. It suggests that PV, PV2, and PV3 are less active than PW12 for the formation of dimethyl ether because the increase in the formal anion charge that accompanies the incorporation of vanadium decreases the Brønsted acidity of the catalysts. In other words, the more negatively charged anions are more basic. Likewise, the two silicon-containing catalysts are less active than their phosphorus analogs but not as much as this point-charge model would predict. We have hestitated to include the results for PV14 in Fig. 15 because we do not believe that it retains its initial structure under reaction conditions. We note that the model would predict for it an exceedingly small turnover rate for dehydration, consistent with the fact that we could detect no dimethyl ether among its products.

The strong dependence of selectivity on vanadium content shown in Fig. 11 occurs because incorporation of vanadium into the Keggin framework increases the fraction of methanol that is oxidized to formaldehyde (a linear function of the number of vanadium ions) and simultaneously decreases the fraction that ends up as dimethyl ether (an exponential function of the number of vanadium ions). Although the exponential dependence suggests that the term "structure sensitive" applies more to the dehydration reaction than the oxidative dehydrogenation, neither functionality need implicate a change in molecular structure or coordination geometry.

Since the samples were limited to those prepared from sodium salts, we cannot comment on any influence that the cations might have exerted. Moreover, given that the vanadium ions in the samples most likely all occupied sites having the same coordination environment—edge-sharing octahedra with one terminal oxo group—our kinetics and characterization data cannot directly afford information concerning the importance of the geometry of that site. Thus, our data do not necessarily contradict conclusions based on the surface anisotropy of the conversion of methanol (*1–7, 45, 46*) since we could not access the same range of coordination geometries or lattice defects that may play important roles in the reactivities of the surfaces of bulk crystals. Moreover, our data do not necessarily contradict the conclusions reached by Niwa *et al.* (*10*) who have suggested that N_f/M does depend on the surface concentration of the metal species, M (Mo in their experiments). For example, by varying the loading in their samples, Niwa *et al.* note that they may also have varied the ratio of Mo ions in sixfold and fourfold coordination, each of which might have different reactivities.

Similarly, our data do not directly afford information about the participation of bridging or terminal oxygens in the oxidative dehydrogenation reaction. We are inclined, however, to side with the recent suggestion by Deo and Wachs (*47*), who have inferred from support effects and from Raman spectroscopy (*48*) that the reaction involves only the bridging oxygens. Our prejudice is also conditioned by the infrared spectra measured by Eguchi *et al.* (*24*), Mizuno *et al.* (*49*), and Brückman *et al.* (*50*), who found that partial reduction of the Keggin structure decreases the intensities of the ν_3 and ν_4 bands (M–O–M stretches) but does not as greatly affect the ν_2 band associated with the terminal M=O bonds. Evidence for the greater liability of the bridging oxygen has also been presented by Neumann and Levin (*43*), Farneth *et al.* (*51*), and Kawafune (*52*), who found that stoichiometric reduction of Keggin ions extracted bridging oxygens from the framework. The near equality of N_f/V measured for our samples in which the vanadium had either silicon or tungsten as next nearest neighbors is consistent with the refractory nature of both silicon and tungsten oxide (*39, 47*).

On the other hand, our results obtained within the constraints of the Keggin structure do caution against any extrapolation to vanadium of the suggestion by Allison and Goddard from GVB calculations that activation of methanol requires two adjacent dioxo metal ions (*53*). All of the metal ions in the Keggin anion are coordinated to a single terminal oxygen. Moreover, we found that the Keggin structure was active for the oxidative dehydrogenation reaction when it contained just a single vanadium ion, the others being tungsten ions which are much less easily reduced. In addition, we found no special reactivity for the catalyst prepared from the lacunary ion, PW11, even though it does have two adjacent metal ions each coordinated to two terminal oxygens. Of course, the lacunary ion does not provide an unequivocal test of the "dual dioxo site" since the metal ions in that case were again tungsten.

CONCLUSIONS

The strategy of using such oxide clusters to control the structure of surface moieties has been employed previously by a number of groups (*50, 54–57*). The last reference is a study very similar to ours in which the oxidative dehydrogenation of methanol was catalyzed by $H_{3+n}[PMo_{12-n}V_nO_{40}]$, both unsupported and supported on the potassium salt of the permolybdenum Keggin ion. Two advantages accrue from the use of the tungsten analogs reported here. First, syntheses and characterization techniques are available to ensure that the substitutions are done in a way that ensures purity of the positional isomers. Second, N_f can be attributed more cleanly to the activity of the vanadium ions alone since, as has been shown, the parent tungsten clusters principally exhibit activity for acid catalysis and are significantly less active for redox catalysis than are the permolybdenum analogs.

We have also exploited a simplification in the product distribution that accompanied the use of a lower concentration of dioxygen than is typically reported in the literature.

The incorporation of lower valent vanadium ions into the tungsten framework affords control over the charge density at the surface of the catalysts and affects their acidity as much as does variation of the heteroatom or exchange of the charge-compensating cations (*27, 50, 58, 59*). A corollary is that the activities and selectivities of catalysts which combine redox and acid functions at the same site ought to be compared cautiously since the average oxidation state of the transition metal ions depends upon the reaction conditions (*60*).

The near constancy of N_f/V for catalysts in which there is good evidence for the persistence and isomeric purity of the vanadium-substituted Keggin ions (in which the number and adjacency of the vanadium ions varied independently) strongly implies that the vanadium ions act independently in the oxidative dehydrogenation reaction under conditions where reoxidation is not rate-limiting. The contrast between this conclusion and the apparent structure sensitivity of the selectivity trends calls to mind the current need in oxidation catalysis for techniques to assay the quantity and nature of surface redox sites in less constrained systems.

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