

Site Titration with Organic Bases During Catalysis: Selectivity Modifier and Structural Probe in Methanol Oxidation on Keggin Clusters**

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Catalytic reactions often require several types of sites with distinct functions, and the relative abundance of these sites influences the rate and selectivity of desired reactions. Heteropolyacid clusters with Keggin structures, which contain acid and redox functions,^[1,2] have recently emerged as interesting catalysts for organic reactions involving bifunctional pathways.

We recently discovered a selective one-step synthesis of dimethoxymethane (CH₃OCH₂OCH₃, DMM, methylal) by oxidation of methanol at low temperatures (453–493 K) on unsupported and SiO₂-supported H_{3+n}PV_nMo_{12-n}O₄₀ (*n* = 0–4) Keggin clusters.^[3] The yields and selectivities (based on the absence of dimethyl ether) of DMM resemble those obtained using supported ReO_x catalysts, the only catalysts that enable the formation of DMM in substantial yields.^[4] Redox and Brønsted acid sites are required for DMM synthesis, and the reaction involves oxidative dehydrogenation of CH₃OH to formaldehyde (HCHO), acid-catalyzed acetalization of CH₃OH/HCHO mixtures, and condensation of hemiacetal or methoxymethanol intermediates (formed in acetalization reactions)^[5,6] with CH₃OH to form DMM.

Brønsted acidity is required to complete the synthesis of DMM, but reaction rates are predominately controlled by the initial formation of HCHO on redox sites, the density and reactivity of which were varied in our studies by changing the dispersion and V/Mo ratio of the Keggin structures, with consequent changes in the rates of DMM synthesis. These compositional changes led to concurrent changes in the number of acid sites, because of the stoichiometry required to balance the charge. DMM selectivity is decreased by side reactions involving CH₃OH dehydration. These reactions are catalyzed by strongly acidic protons in H_{3+n}PV_nMo_{12-n}O₄₀ and lead to the undesired formation of dimethyl ether (DME). The latter product ultimately converts into HCHO and DMM products, and can even re-form CH₃OH, but forms DMM

more slowly than CH₃OH.^[3] Thus, the formation of DME through these side reactions necessitates longer residence times to achieve high yields of DMM from CH₃OH.

We report here the selective titration of protons with organic bases to control the densities of acid sites in Keggin clusters and to measure their dispersion; in both cases we do this during the catalytic reaction, a requirement imposed by the dynamic changes in accessibility that arise from reactions of polar molecules on Keggin clusters.^[1,2] In this manner we are able to measure turnover rates (per exposed Keggin unit; KU) and to control the redox and acid properties independently for a given composition of Keggin cluster. This approach has led to unprecedented DMM selectivities (> 80%) and to a family of stable organic–inorganic composites that provide effective bifunctional catalysts for broad classes of redox–acid bifunctional reactions.

The dispersion of Keggin structures was measured by titration of Brønsted acid sites with a sterically hindered pyridine (2,6-di-*tert*-butylpyridine) during catalytic reactions of mixtures of CH₃OH and O₂. This 2,6-di-*tert*-butylpyridine titrant can protonate Brønsted acid sites, but it cannot interact with Lewis acid sites because of steric constraints near the N atom.^[7] Its essentially hydrophobic character also prevents its dissolution and migration into secondary structures of Keggin clusters. This result is in contrast with more polar pyridine titrants, which dissolve and penetrate into these secondary structures.^[1] Thus, uptake of 2,6-di-*tert*-butylpyridine during CH₃OH reactions (per KU) reflects the number of accessible protons, and for a given H_{3+n}PV_nMo_{12-n}O₄₀ stoichiometry, the fraction of the Keggin structures accessible at external surfaces in supported and unsupported secondary structures. We note that such titrations must be carried out during the reaction, because of the known ability of various reactants to solvate and expose internal regions within secondary packing structures of Keggin clusters to varying degrees.

The number of 2,6-di-*tert*-butylpyridine molecules adsorbed during reactions of CH₃OH and O₂ at 453 K on H₅PV₂Mo₁₀O₄₀/SiO₂ (0.28 KU nm⁻² surface density on SiO₂) increased with time and reached saturation at 1.2 H⁺ per KU after about 12 × 10³ s (Figure 1). This value corresponds to a nominal fractional dispersion of 0.24, on the basis of the expected H⁺/KU stoichiometry; we note, however, that some of the protons in the stoichiometric starting cluster may have been removed during condensation reactions of OH groups in solvated Keggin clusters with silanols on anchoring to SiO₂.

H⁺/KU ratios decreased from 1.6/1 to 0.7/1, which corresponds to a decrease in fractional KU dispersion from 0.32 to 0.15, as the KU surface densities increased from 0.1 to 0.65 KU nm⁻² on H₅PV₂Mo₁₀O₄₀/SiO₂ samples. This value was 0.02 H⁺ per KU for bulk H₅PV₂Mo₁₀O₄₀. The rates of DMM synthesis (per KU) decreased in parallel with this decrease in fractional KU dispersion as the surface density increased from 0.1 to 0.65 KU nm⁻² (Figure 2). This excellent correlation between rates and titrant uptake for all samples, including an unsupported version of this Keggin composition, indicates that 2,6-di-*tert*-butylpyridine predominately titrates those Keggin structures that participate in bifunctional DMM

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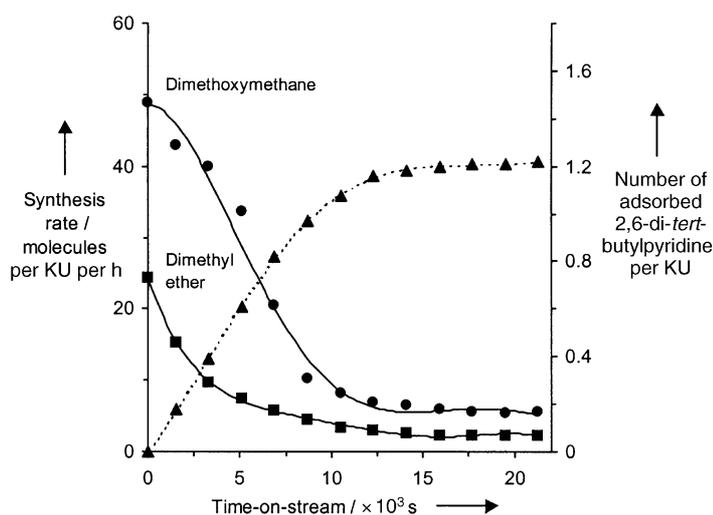


Figure 1. Adsorption uptakes (\blacktriangle) and rates of DMM (\bullet) and DME synthesis (\blacksquare) as a function of time-on-stream during addition of 2,6-di-*tert*-butylpyridine to $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{SiO}_2$ (0.28 KU nm^{-2} , 453 K, 4 kPa CH_3OH , 9 kPa O_2 , $\text{CH}_3\text{OH}/2,6\text{-di-}i\text{-tert-butylpyridine (mol)} = 1110/1$).

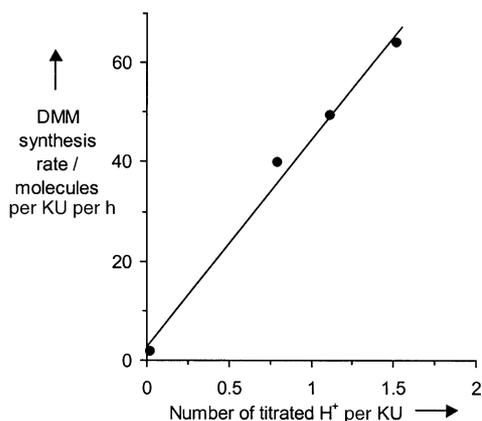


Figure 2. Rates of DMM synthesis as a function of the number of protons (per KU) titrated with 2,6-di-*tert*-butylpyridine on unsupported and SiO_2 -supported ($0.1\text{--}0.65 \text{ KU nm}^{-2}$) $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (453 K, 4 kPa CH_3OH , 9 kPa O_2 , $\text{CH}_3\text{OH}/2,6\text{-di-}i\text{-tert-butylpyridine (mol)} = 1110/1$).

synthesis pathways. A slight inaccuracy arises from the ability of polar CH_3OH reactants to penetrate secondary Keggin structures to a small extent, as we discuss below.

The rates (per KU) for both the bifunctional DMM and monofunctional DME pathways decreased as the 2,6-di-*tert*-butylpyridine titrated the H^+ sites in $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{SiO}_2$ (Figure 1); they reached non-zero constant values after saturation adsorption of 2,6-di-*tert*-butylpyridine (1.2 H^+ per KU; Figure 1), probably because CH_3OH can continue to reach a small number of protons that are inaccessible to 2,6-di-*tert*-butylpyridine (ca. 10–15%). The titration of protons led to lower DME selectivities, but the small number of residual protons not reached by 2,6-di-*tert*-butylpyridine prevents the attainment of DME selectivities lower than 25%. Therefore, we chose instead to examine the effect of titration with pyridine, which can penetrate secondary Keggin

structures;^[1] this property makes it unsuitable for KU dispersion measurements, but a more effective titrant to suppress residual pathways leading to DME synthesis.

Figure 3 shows the rates of DMM and DME synthesis at 453 K and their ratio on $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{SiO}_2$ (0.1 KU nm^{-2}) as a function of the number of H^+ sites per KU titrated by pyridine. The products HCHO and methyl formate (MF) were detected at low selectivities (< 4%) and these data are not included in the figures. Titration with pyridine during the reaction decreased the rates of both DME and DMM synthesis, but the ratio of the DMM/DME rates increased from 1.9/1 to 7.5/1 as the number of titrated protons increased from 0 to 0.6 H^+ per KU. In effect, the loss of acid sites by titration of 0.6 H^+ per KU led to small changes in the rates of DMM synthesis (from 63.9 to $49.9 \text{ KU}^{-1}\text{h}^{-1}$), but decreased the rates of DME synthesis by more than a factor of five (34.2 to $6.6 \text{ KU}^{-1}\text{h}^{-1}$; Figure 3). Both DME and DMM reaction products became undetectable after titration of about 2.0 H^+ per KU, thus confirming that all the sites accessible to the reactants are titrated by pyridine.

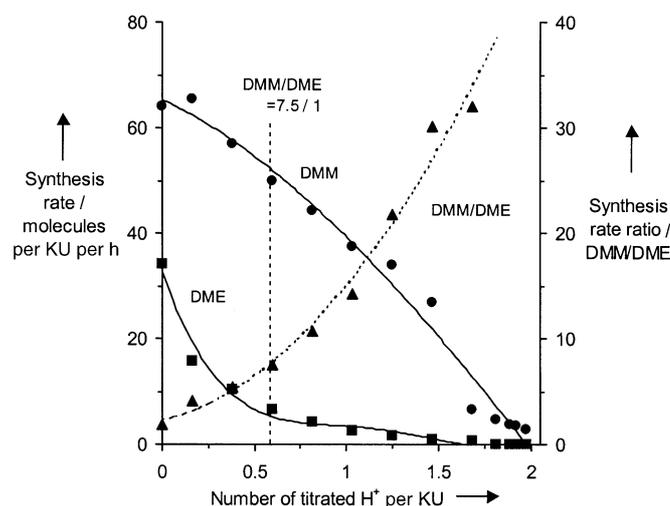


Figure 3. Rates of DMM (\bullet) and DME synthesis (\blacksquare) and their ratios of DMM/DME (\blacktriangle) as a function of the number of protons (per KU) titrated with pyridine on $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{SiO}_2$ (0.1 KU nm^{-2} , 453 K, 4 kPa CH_3OH , 9 kPa O_2 , $\text{CH}_3\text{OH}/\text{pyridine (mol)} = 800/1$).

These data confirm that the number of Brønsted acid sites can be systematically controlled by partial titration of Keggin structures during reaction, which has marked and beneficial consequences for the selectivity of bifunctional redox–acid catalytic reactions. Selectivities can be modified significantly and, as we discuss shortly, permanently, over the time-scale of typical catalytic use. In the catalytic system used in this proof-of-concept study, the acid-catalyzed steps (acetalization and condensation) required for bifunctional reactions leading to DMM synthesis are near thermodynamic equilibrium, while redox pathways leading to HCHO intermediates limit the overall rates of DMM synthesis.^[3] In contrast, CH_3OH dehydration reactions leading to DME are far from equili-

brium and monofunctional in character; thus, they are much more strongly influenced by the number of available Brønsted acid sites, which can be accurately, flexibly, and permanently controlled by titration with organic bases during the reaction.

These specific results for $H_5PV_2Mo_{10}O_{40}/SiO_2$ are representative of those obtained for all V/Mo ratios (0–0.5/1) and KU surface densities and dispersions (Table 1). In all cases, the titration of 0.5–0.9 H^+ per KU with pyridine significantly decreased the rates of DME synthesis (by factors of 4.5–8), while only slightly decreasing the rates of DMM synthesis (by factors of 1.2–1.3); these combined effects led to much greater DMM selectivities (DMM/DME ratios > 6/1) than on each corresponding composition unmodified by pyridine titrants (DMM/DME ratios ca. 2/1). These titration methods led to organic–inorganic composite materials with unprecedented selectivity to DMM (> 80%) and extremely low DME (< 12%) selectivity, without any significant decrease in DMM yields over those obtained without pyridine titrants.

Table 1: Rates of DMM and DME synthesis and ratios of DMM/DME rate on SiO_2 -supported $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n=0, 1, 2, 4$; ca. 0.1 KU nm^{-2}) and $H_5PV_2Mo_{10}O_{40}/SiO_2$ with varying surface densities of Keggin units (KU; $0.1\text{--}0.65 \text{ KU nm}^{-2}$) before and after titration of 0.5–0.9 H^+ per KU.^[a]

Catalyst [KU nm^{-2}]	Before titration [molecules $\text{KU}^{-1} \text{ h}^{-1}$]			After titration [molecules $\text{KU}^{-1} \text{ h}^{-1}$]		
	DMM	DME	DMM/ DME	DMM	DME	DMM/ DME
$H_3PMo_{12}O_{40}$ (0.1)	60.7	35.7	1.7/1	43.1	7.0	6.2/1
$H_4PVMo_{11}O_{40}$ (0.1)	72.6	31.5	2.3/1	51.7	6.4	8.1/1
$H_5PV_2Mo_{10}O_{40}$ (0.1)	63.9	34.2	1.9/1	49.9	6.6	7.5/1
$H_6PV_4Mo_8O_{40}$ (0.1)	43.4	20.7	2.1/1	33.5	4.7	7.1/1
$H_5PV_2Mo_{10}O_{40}$ (0.28)	49.3	25.4	1.9/1	39.8	6.2	6.4/1
$H_5PV_2Mo_{10}O_{40}$ (0.65)	40.8	26.1	1.6/1	27.2	3.1	8.8/1

[a] 453 K, 4 kPa CH_3OH , 9 kPa O_2 , $CH_3OH/pyridine$ (mol) = 800/1, balance He; ca. 17–22% CH_3OH conversion.

Finally, we established the permanence of these titrant–KU complexes during extended catalytic reactions of CH_3OH and O_2 at 453 K. Figure 4 shows the rates of DMM and DME synthesis on $H_5PV_2Mo_{10}O_{40}/SiO_2$ (0.1 KU nm^{-2}) for a period of 15 h after removal of pyridine from the inlet stream; these data were obtained after about 0.6 H^+ per KU titration by pyridine. The rates of DMM and DME synthesis did not change during catalytic reactions of CH_3OH and O_2 over this period of time. We conclude, therefore, that pyridine–KU hybrid structures remain unchanged during the reaction, and that titration is permanent at these reaction conditions. Similar stability was confirmed for other compositions of

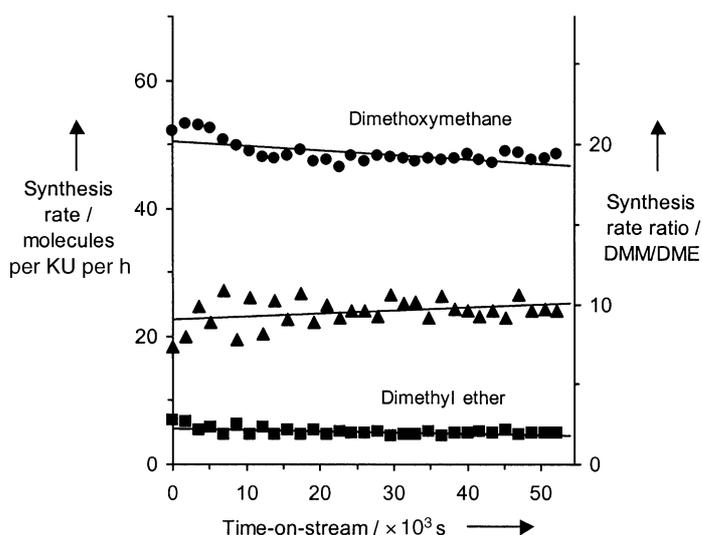


Figure 4. Rates of DMM (●) and DME synthesis (■) and their ratios of DMM/DME (▲) as a function of time-on-stream after titration of 0.6 H^+ per KU and stop of pyridine injection on $H_5PV_2Mo_{10}O_{40}/SiO_2$ (0.1 KU nm^{-2} , 453 K, 4 kPa CH_3OH , 9 kPa O_2 , $CH_3OH/pyridine$ (mol) = 800/1).

Keggin structures; it is consistent with the strong interaction between pyridine rings and protons in Keggin structures detected by temperature-programmed desorption in this study, and from infrared spectra and thermal desorption data in previous studies.^[8,9]

These stable organic–inorganic composites represent a novel class of materials that have significant implications for selectivity control in bifunctional redox–acid catalysis. Pyridine has been used to measure the number of available acid sites in fresh samples (not during catalytic reactions),^[8–10] but we have found no previous studies describing the intentional use of organic bases as selectivity modifiers for these types of materials. Pyridine–KU complexes have been previously synthesized in efforts to form secondary Keggin structures, for which subsequent removal of pyridine during thermal treatments and before reaction may lead to specific pore morphologies or reduced addenda atoms.^[11,12]

In summary, the selective and permanent titration of protons with organic bases (2,6-di-*tert*-butylpyridine or pyridine) provides an accurate measure of the dispersion of Keggin structures during catalysis and absolute values for the turnover rates of CH_3OH oxidation. This method also led to the independent and systematic control of redox and acid properties in $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n=0\text{--}4$) Keggin clusters and to unprecedented DMM selectivities (> 80%) and yields. This approach provides a novel and effective general framework for the in situ design of hybrid organic–inorganic catalysts for chemical reactions requiring controlled densities and reactivities of redox and acid sites. It appears to be generally applicable to reactions that take place at temperatures below those required for the desorption of the chosen titrant. Our current studies aim to extend these methods to bifunctional reactions of alkanes, alkenes, and higher alcohols, which often involve multiple redox, acidic, and basic catalytic functions.

Experimental Section

Supported heteropolyacid catalysts were prepared by incipient wetness impregnation of SiO₂ (Cab-O-Sil, 288 m² g⁻¹) with methanolic (Merck, 99.98 %) solutions of H_{3+n}PV_nMo_{12-n}O₄₀·30H₂O (*n* = 0, 1, 2, 4; Japan New Metals Co.) at 298 K for 5 h, followed by drying in ambient air at 398 K overnight.

Methanol and titration reactions were carried out at 453 K in a fixed-bed quartz microreactor containing catalyst powders (0.1–0.3 g). Samples were treated in flowing 20 % O₂/He (O₂, Praxair, 99.999 %; He, Airgas, 99.999 %; 0.67 cm³ s⁻¹) at 553 K for 1.0 h before catalytic reaction measurements. The Keggin structures of these materials before and after the thermal treatment were characterized by Raman spectroscopy.^[3] No structural changes were detected for thermal treatments below 673 K. The reactant mixture consisted of 4 kPa CH₃OH (Merck, 99.99 %), 9 kPa O₂, 1 kPa N₂ (Praxair, certified O₂/N₂ mixture), and 86 kPa He (Airgas, 99.999 %). Methanol or mixtures of methanol with pyridine (Fisher Scientific, 99.9 %) or 2,6-di-*tert*-butylpyridine (Aldrich, 97 %) at a molar ratio of CH₃OH/pyridine = 800/1 or CH₃OH/2,6-di-*tert*-butylpyridine = 1110/1 were introduced by continuous injection using a syringe pump. Reactants and products were analyzed by on-line gas chromatography (Hewlett-Packard 6890GC) using a methylsilicone capillary column and a Porapak Q packed column connected to flame-ionization and thermal conductivity detectors, respectively. Rates are reported as the number of CH₃OH molecules converted into a given product per Keggin unit per hour.

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