

## Effects of Composition on the Reactivity of Protons in Polyoxometalate Clusters

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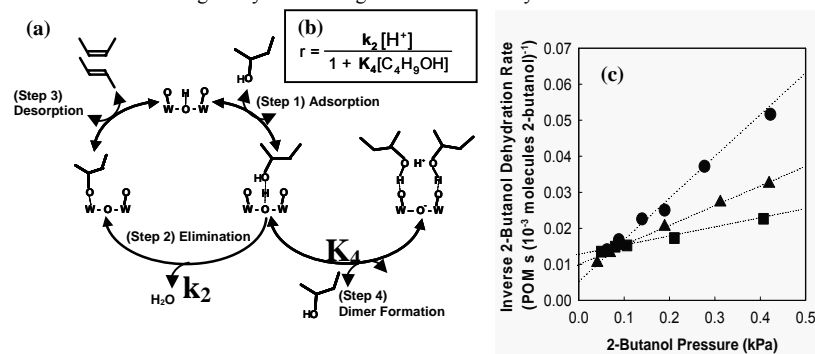
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Polyoxometalate (POM) clusters provide well-defined atomic connectivity and cluster size, as well as compositional flexibility; as a result, they are excellent models to determine structure-function relations in catalysis by dispersed oxides. We report here the effects of the central atoms X (P, Si, Al, Co), charge-balancing cations C (Cs, Na), and POM surface density on the reactivity of protons in  $C^{m+}_yH_{8-n-m}X^{n+}W_{12}O_{40}$  Keggin-type clusters supported on  $SiO_2$ , for the specific case of 2-butanol dehydration catalyzed by Brønsted acid sites. Accessibility constraints imposed by secondary structures were minimized by supporting POM clusters on  $SiO_2$  at surface densities of 0.04 – 0.5 POM  $nm^{-2}$ . Catalytic data are compared with density functional theory (DFT) estimates of reaction constants to confirm the proposed elementary steps and to provide insights into the effects of the electronic properties of Keggin clusters on acid strength and proton reactivity.

A plausible sequence of elementary steps is shown in Figure 1(a). It includes 2-butanol adsorption on Brønsted acid sites (step 1), irreversible decomposition of adsorbed 2-butanol via  $H_2O$  elimination (step 2), reversible desorption of butene (step 3), and quasi-equilibrated formation of 2-butanol dimers (step 4), with step 2 as the kinetically-relevant step. The rate constant for 1-butene isomerization is much larger than the 2-butanol dehydration rate constant  $k_2$  (see rate equation shown in Figure 1(b)), indicating that desorption of butoxide intermediates (step 3), required for isomerization and dehydration turnovers, does not limit 2-butanol dehydration rates. DFT calculations indicate that the preferred reaction path occurs through a cationic transition state in the elimination reaction to form an adsorbed butoxide (step 2) and  $H_2O$ . The charged nature of the transition state led to alcohol dehydration rate constants  $k_2$  that were strongly affected by the identity of the alcohol and increased with the level of substitution at the carbon bearing the OH group ( $k_{1-butanol} : k_{2-butanol} : k_{tert-butanol} = 1 : 2000 : 1 \times 10^5$  (343 K)). Measured 2-butanol dehydration rates were inversely proportional to 2-butanol pressure (Figure 1(c)), because of the quasi-equilibrated formation of unreactive 2-butanol dimers ((step 4), Figure 1(a)). The formation of unreactive alcohol dimers was also reported for ethanol dehydration on bulk  $H_3PW_{12}O_{40}$  [1]. The rate constant of C-O bond breaking ( $k_2$ ) and the equilibrium constant for the formation of unreactive dimers ( $K_4$ ) can be obtained from the proposed rate equation and the measured dehydration rates ((Figure 1(b) and (c)). The number of accessible protons  $[H^+]$ , necessary to extract  $k_2$  values from these data, was measured by titration with 2,6-di-tert-butylpyridine; these measurements were carried out during catalytic reactions, because the identity of reactants and products influences the accessibility of protons within secondary POM structures.

Neither  $k_2$  nor  $K_4$  were affected by POM surface density (0.04 – 0.5 POM  $nm^{-2}$ ). Both  $k_2$  and  $K_4$  increased monotonically with increasing valence of the central atom. These changes reflect a concurrent decrease in the charge of POM clusters and in the number of

protons required for charge balance. These trends are consistent with the expected increase in acid strength when the conjugate base (the negatively charged oxide cluster) becomes weaker as the amount of negative charge to be delocalized decreases. The replacement of some of  $H^+$  in POM clusters with less electronegative cations ( $Cs^+$ ,  $Na^+$ ) decreased both  $k_2$  and  $K_4$ , because their lower electronegativity leads to higher electron density within POM clusters.



**Figure 1(a).** Proposed sequence of elementary steps for 2-butanol dehydration. **(b)** Rate equation for 2-butanol dehydration on  $C^{m+}_yH_{8-n-m}X^{n+}W_{12}O_{40}$ . **(c)** Inverse 2-butanol dehydration rates as a function of 2-butanol pressure on silica supported  $H_3PW_{12}O_{40}$  (●),  $H_4SiW_{12}O_{40}$  (▲), and  $H_5AlW_{12}O_{40}$  (■) (343 K, 0.04 POM  $nm^{-2}$ , conversion < 10%).

DFT simulations support the proposed mechanism and the trends observed with changes in POM composition (Table 1). Specifically, theory predicts a decrease in the C-O

**Table 1. Proton Affinities, activation and dimer formation energies for different central atoms.**

Catalyst	Proton Affinity <sup>1</sup>	$E_{activation}$ <sup>2</sup>		$\Delta H_{dimer}$ <sup>3</sup>	
		Exp.	Calc.	Exp.	Calc.
$H_3PW_{12}O_{40}$	1087	108	132.4	69	83.7
$H_4SiW_{12}O_{40}$	1105	110	140.0	66	76.7
$H_5AlW_{12}O_{40}$	1125	112	145.8	62	70.3

<sup>1</sup> defined as  $-\Delta H_{rxn}$  of  $A^- + H^+ \rightarrow HA$  ( $A^-$  is the conjugate base, and HA is the acid) calculated by DFT

<sup>2</sup> activation energy of step (2); <sup>3</sup> dimer formation energy (step (4) (Figure 1(a))

catalysts require a subtle balance between the parallel effects of proton affinity on  $k_2$ , which increases rates, and  $K_4$ , which decreases reaction rates.

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### References

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