According to Scheme 1, the rate of 2-butanol dehydration may be expressed as:

$$r = k_2[C_4H_9OH]_{ads} \quad \text{(Eq. 1)}$$

which, in terms of the gas-phase concentrations of the reactants and products, becomes:

$$r = \frac{k_2 \frac{k_1}{(k_{-1} + k_2)} [C_4H_9OH][H^+]}{1 + \frac{k_1}{(k_{-1} + k_2)} [C_4H_9OH] \left(1 + \frac{k_2}{k_3} + K_4[C_4H_9OH] + K_5[H_2O]\right) + \frac{k_{-3}}{k_3} [C_4H_8]} \quad \text{(Eq. 2)}$$

The first term in the denominator can be omitted assuming that the most abundant surface species are the 2-butanol monomers \(\frac{k_1}{(k_{-1} + k_2)} [C_4H_9OH]\) (2\(^{nd}\) denominator term) and 2-butanol dimers \(\frac{k_2}{(k_{-1} + k_2)} [C_4H_9OH]^2\) (4\(^{th}\) denominator terms).

The 3\(^{rd}\) term \(\frac{k_1}{(k_{-1} + k_2)} \frac{k_2}{k_3} [C_4H_9OH]\) may be omitted because the desorption of butoxy intermediates is fast \((k_3>k_2)\), while the remaining two denominator terms \(\frac{k_{-3}}{k_3} [C_4H_8] + \frac{k_1}{(k_{-1} + k_2)} K_5[H_2O]\) corresponding to butene and water readsorption (formation of the 2-Butanol/H_2O dimer) may be neglected at low conversions (low C_4H_8 and H_2O pressures).

So, with 2-butanol monomers and 2-butanol dimers as most abundant surface species and at low conversions, Eq. 2 becomes:

$$r = \frac{k_2[H^+]}{1 + K_4[C_4H_9OH]} \quad \text{(Eq. 3)}$$

with a linear dependence of the inverse rate on the 2-butanol pressure.

$$r^{-1} = \frac{1}{k_2[H^+]} + \frac{K_4}{k_2[H^+]} [C_4H_9OH] \quad \text{(Eq. 4)}$$
**H₃PW₁₂O₄₀:** Intact P-containing POM clusters were supported on silica. The $^{31}$P MAS NMR spectra for bulk H₃PW and silica supported H₃PW in the surface density range of 0.04 – 0.5 POM nm⁻² showed only a line at about – 15 ppm (H₃PO₄ as external reference), assigned to the intact Keggin structure¹. Partly decomposed (lacunary) Keggin structures would have given rise to a $^{31}$P NMR signal at about -13.3 ppm,² which is not detected here.

**H₅AlW₁₂O₄₀:** The synthesized H₅AlW₁₂ was characterized by IR and $^{27}$Al-NMR (AlCl₃ x 6H₂O as external reference $\delta = 0$ ppm).

IR (in cm⁻¹) observed: 976(s), 914(s), 766(br, s) [740-820], 538(m), 480(s); lit³: 972(s), 899(s), 807(vs), 795(br, s); 747 (br, s); 538 (m), 477 (m).

$^{27}$Al-NMR (D₂O): 72.12, 71.76 ppm; literature: 72.1 and 71.6 ppm for $\alpha$ and $\beta$ isomers. The $^{27}$Al-MAS NMR of supported 0.04H₅AlW/Si showed a peak at 70.4 ppm with a shoulder at 70.7 ppm (s). No peak in the range of 60 - 70 ppm was observed confirming the absence of lacunary species.

**H₆CoW₁₂O₄₀:** The synthesized H₆CoW₁₂ was characterized by potentiometric titration with Cs₂CO₃ (6 H⁺/Keggin molecule) and IR. IR (in cm⁻¹) observed: 958(s), 884(s), 736(s,br), 451(s); lit⁴: 960, 895, 738, 445 cm⁻¹.

**Reaction:** Janik et al.⁵ used density functional theory to show that the partial decomposition of HₙXM₁₂O₄₀ via HₙXM₁₂O₄₀ ↔ Hₙ₋₂XM₁₂O₃₉ + H₂O is a function of temperature and water partial pressure. We note that the dehydration reaction of 2-butanol carried out at low temperatures (343 K) with the reaction product H₂O is thus ideally suited to ensure the structural integrity.

**Impregnation Solvent:** CH₃CH₂OH instead of H₂O was used as the impregnation solvent for the preparation of SiO₂ supported H₈₋₆Xⁿ⁺W. The lower heat of proton solvation H⁺solv of CH₃CH₂OH compared to H₂O⁶ leads to a stabilization of the Keggin anion according to:

\[
23H_3^{+}\text{solv} + [\text{HPO}_4]^{2-} + 12[\text{WO}_4]^{2-} \leftrightarrow [\text{PW}_{12}\text{O}_{40}]^{3-} + 12\text{H}_2\text{O}
\]

---