Porous ionic crystals composed of Nb/W mixed-addenda polyoxometalates as solid base catalysts

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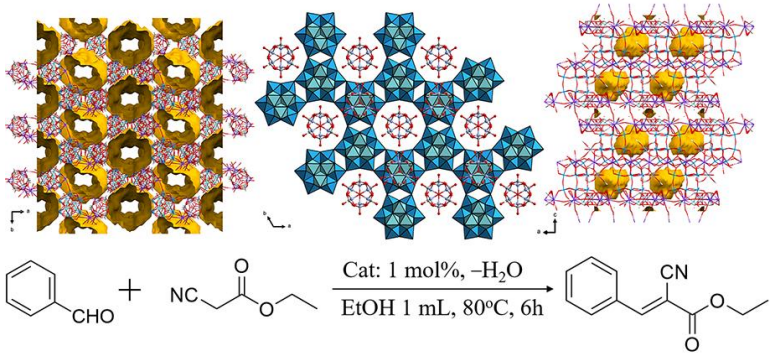
Polyoxometalates (POMs), which are robust, discrete, and structurally well-defined oxide cluster anions, are widely used as acid and oxidation catalysts, while base catalysis of POMs remains an ongoing challenge. It has been reported that POMs composed of group V elements (V, Nb, Ta) act as base catalysts in CO_2 fixation and Knoevenagel reactions because the surface oxygen atoms become more basic with an increase in the negative charges.[1] We have been working on the design, synthesis and functions of porous ionic crystals (PICs), which are crystalline porous composites of POMs with macrocations,[2] while there are no reports of Nb containing PICs.

In this work, three PICs composed of Dawson-type Nb/W mixed-addenda POMs of mono-substituted $[P_2W_{17}(NbO_2)O_{61}]^{7-}$ or tri-substituted $[P_2W_{15}(NbO_2)_3O_{59}]^{9-}$ with $[Cr_3O(OOCH)_6(H_2O)_3]^+$ ($K_5H[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{17}NbO_{62}](NO_3)\cdot 34H_2O$, **1**; $K_5[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{17}NbO_{62}]\cdot 18H_2O$, **2**; $K_6H[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{15}(NbO_2)_3O_{59}]\cdot 17H_2O$, **3**) were synthesized and tested in Knoevenagel condensation. As a result, **3** exhibited the highest yield (78%) and selectivity (99%) with good reusability, showing that the substitution of W with Nb leads to increased catalytic activity. Furthermore, the catalytic mechanism was studied with ^{31}P solid-state NMR, which indicated that the exposure of terminal oxygen atoms of Nb to the pore surface is crucial to the catalytic performance.



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