V group metal oxide clusters on base catalytic property

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Keywords: Polyoxomethalate; Group V metal oxide cluster; Base catalysis, Knoevenagel condensation reactions

Polyoxometalates with group V transition metals have been studied as base catalysts for Knoevenagel condensation (KC) reactions. Very recently, we demonstrated the superbase catalysis of Lindqvist-type polyoxoniobates, $[Nb_6O_{19}]^{8-}$, complexed with tetrabutylammonium (TBA) cations (**TBA-Nb6**).[1] From density function theory (DFT) calculations, polyoxotantalates such as $[Ta_6O_{19}]^{8-}$ are expected to show a higher negative natural bonding charge than polyoxoniobates,[2] suggesting the higher base catalysis properties of polyoxotantalates than polyoxoniobates. In this study, we synthesized TBA salt of $[Ta_6O_{19}]^{8-}$ (**TBA-Ta6**) and **TBA-Nb6** by the microwave-assisted hydrothermal method,[3] characterized their basic properties by indicator titration method, and investigated their base catalytic activities. Table 1 shows the color change of indicators (phenolphthalein, 2,4-dinitroaniline, 4-chloro-2-nitro aniline, 4-nitroaniline, and 4-chloroaniline) after adding the equimolar of the **TBA-Nb6** and **TBA-Ta6** (5 μmol). The results indicate that the **TBA-Nb6** and **TBA-Ta6** have basic sites having pK_a up to 26.5. As for the catalytic activity, the **TBA-Ta6** was found to be a homogeneous catalyst of KC reactions at high pK_a for benzaldehyde (BA) and nitriles; 4-methoxy phenylacetonitrile (pK_a = 23.8), and phenoxyacetonitrile (pK_a = 28.1). The **TBA-Ta6** showed higher yields in the KC reaction at pK_a = 28.1 than the **TBA-Nb6** (Fig. 1). These base indicators titration and catalytic reaction suggest the stronger basic properties of the **TBA-Ta6** than **TBA-Nb6**, consistent with the higher negative natural bonding charge from the DFT calculations

Table 1. Color change of base indicators after adding **TBA-Nb6** and **TBA-Ta6.**

Sample	pK_a 9.3	15	17.2	18.4	26.5
Blank					
TBA-Nb6					
TBA-Ta6					

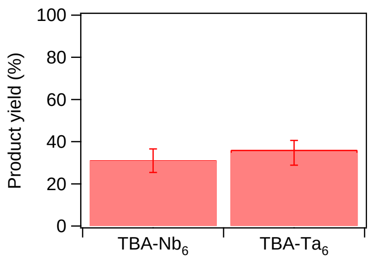

Fig. 1. Yield products of KC reaction using **TBA-Nb6** and **TBA-Ta6** as catalysts at pK_a 28.1 (30°C).

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