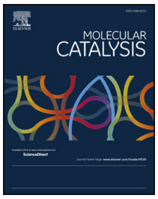
Molecular Catalysis 453 (2018) 93–99

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat



Polyoxoniobates as a superior Lewis base efficiently catalyzed Knoevenagel condensation

Qiaofei Xu, Yanjun Niu, Guan Wang, Yingguang Li, Yuan Zhao, Vikram Singh, Jingyang Niu*, Jingping Wang*

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecule and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

ARTICLE INFO

Keywords:
Polyoxoniobates
Base catalysis
Knoevenagel condensation
Natural population analysis

ABSTRACT

The outstanding basicity of negative charged Lindqvist type Polyoxoniobate $K_7HNb_6O_{19}{\cdot}13H_2O$ (Nb_6) have been proved experimentally as well as by theoretical NBO calculations, the results insights high electron density on terminal and bridging oxygen atoms of niobate anion. The most negative Natural Bond Orbital charge (NBO) of oxygen in Nb_6 is -1.001, which is a much more negative value than those reported in other polyoxometalates, that corroborates its high basicity thus likely to be employed as a strong base catalyst. Experimental study suggests that Nb_6 can efficiently catalyze Knoevenagel condensation of various carbonyl compounds with active methylene compounds neglecting the steric and electronic effect of aromatic aldehydes under mild conditions. Kinetic test shows that Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate exhibits second-order kinetics in the presence of Nb_6 and the calculated activation energy is 43.3 kJ mol^{-1}. Meanwhile, a proper mechanism according to the NBO study speculates that the most negative charged terminal oxygens in Nb_6 would be pivotal in this transformation.

1. Introduction

Olefination is one of the most fundamental reactions where the products exert enormous importance on organic synthesis [1]. As a kind of C=C bonds-forming reactions, Knoevenagel condensation reaction is a crucial method to produce olefins using active methylene group reactivity with diverse functional groups via the coupling reaction of carbonyl compounds in the presence of base catalysts along with the loss of molecular H_2O in the suitable reaction conditions. This reaction is of prime importance in many significant areas of research like synthesis of various reaction intermediates, products for perfumes, calcium antagonists, polymers and in pharmaceutical industries [2,3]. Traditionally, the solid bases [4,5], Lewis acids [6,7], and organometallic compounds [8,9] were applied as catalysts in the process, while they are lack in their efficiency, robustness, and recyclability [10]. Therefore, considerable research efforts have been focused on this reaction by using various catalysts, such as metal-organic frameworks [11,12], ionic liquid [13], molecular complexes [14] and etc.

Polyoxometalates (POMs) as a class of anionic metal-oxide clusters mainly obtained by the condensation reaction of corresponding oxysalts or metallic oxides. Structurally, POMs are constructed by the corner-, edge-, or face-shared fashion of metal oxide polyhedral (MO_x: M = W^{VI}, Mo^{VI}, V^{V}, Nb^{V}, Ta^{V}, etc., and x = 4–7), thus leading to provides novel building units for the assembly of larger systems [15–17]. Moreover, POMs have exhibited remarkable performance in many fields, such as fluorescence [18], magnetism [19], drugs [20], electrochemistry [21], and especially in catalysis [22–25]. To date, many applications involving POMs incorporated V^{V}, Mo^{VI}, and W^{VI} were investigated in various types of catalytic reactions including acid catalysis [26–29], oxidation catalysis [30–34], photocatalysis [35–37] and electro-catalysis [38–41] mainly due to their redox tunable behavior, low pH stability, high thermal resistivity and photoelectric behaviors [42]. However, there were few reports which deals on the basic catalytic performance of POMs [43–45]. In general, it is well known that POMs possess strong acidity thus the weak basicity of their conjugate base restricts to support them as outstanding base catalysts. Actually, outstanding works on Knoevenagel condensation reaction have shown that polyoxotungstates (POTs) exhibited fascinating performance in this process. Mizuno et al. firstly reported the superior catalytic reactivity of alkaline disilicoicosatungstates $[H(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{7-}$ than the acidic di $[\{\gamma\text{-}SiW_{10}O_{32}(H_2O)_2\}_2(\mu\text{-}O)_2]^{4-}$ for Knoevenagel condensation reaction in the similar reaction conditions[46]. Subsequently, Mizuno and coworkers revealed that $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$can act as an efficient base catalyst for Knoevenagel condensation [47]. Later, Song et al. also

---

* Corresponding authors.
E-mail addresses: jyniu@henu.edu.cn (J. Niu), jpwang@henu.edu.cn (J. Wang).

https://doi.org/10.1016/j.mcat.2018.05.002
Received 9 March 2018; Received in revised form 23 April 2018; Accepted 3 May 2018

explored highly charged tri-lacunary polyanoins i.e. $Na_8H[A\text{-}PW_9O_{34}]$ and $Na_8H[B\text{-}PW_9O_{34}]$ as catalysts for cyanosilylation and Knoevenagel condensation reactions, respectively [48]. Beside these, it is well documented that POTs supported on graphene oxide [49] and LDH (Layered double hydroxides) [50] also show excellent performance as the catalyst for Knoevenagel condensation. However, polyoxoniobates (PONs) as an important subclass of POMs have been investigated relatively in synthetic chemistry but it is seldom explored in catalysis. Hence, it is significant to open a new way for their applications in catalytic direction.

According to literatures, more electronegative oxygen atoms provide higher basicity in POMs, which could be approximately deduced by comparison of their "charge-density" as: Charge-density (charge/atom) = (anionic charge of the POM)/(number of non-hydrogen atoms of the POM) [51,52]. From the charge-density of conventional PONs and POTs: $[Nb_6O_{19}]^{8-}$ (0.32), $[Ti_2Nb_8O_{28}]^{8-}$ (0.21), $[Nb_{10}O_{28}]^{6-}$ (0.16), $[SiNb_{12}O_{40}]^{16-}$ (0.30), $[(PO_2)_3PNb_9O_{34}]^{15-}$ (0.28), $[H_2Si_4Nb_{16}O_{56}]^{14-}$ (0.18), $[W_6O_{19}]^{2-}$ (0.08), $[SiW_{12}O_{40}]^{4-}$ (0.075), $[SiW_{11}O_{39}]^{8-}$ (0.16), $[PW_9O_{34}]^{9-}$ (0.20), it is obvious that PONs possess higher charge-density than POTs. However, to date, only two works were reported on PONs catalyzed Knoevenagel condensation reaction: Tsukuda et al. reported that the $(TMA)_6[Nb_{10}O_{28}]$ can be regarded as an efficient base catalyst for this process [51]; Wang et al. discovered $Na_{16}[SiNb_{12}O_{40}]$ as a base catalyst for catalyzing CO_2 cycloaddition and Knoevenagel condensation [53]. Notably, $[Nb_6O_{19}]^{8-}$ shows the highest charge-density in these compounds including $[SiNb_{12}O_{40}]^{16-}$ and $[Nb_{10}O_{28}]^{6-}$, which suggests the wonderful basicity of $[Nb_6O_{19}]^{8-}$ which facilitates them as the best candidates for Knoevenagel condensation reaction. In addition, $K_7HNb_6O_{19}\cdot 13H_2O$ (Nb_6) is easily prepared with high yield, which may provide the potential catalytic use in its application.

Herein, we employed Nb_6 as a base catalyst in Knoevenagel condensation reaction, which exhibited excellent catalytic performance for the condensation of various aldehydes and ketones at mild reaction conditions. Furthermore, theoretical calculation for the basicity of $[Nb_6O_{19}]^{8-}$ and the comparison with other POMs (including PONs and POTs) was also executed by density functional theory (DFT). On the basis of DFT calculations results, it can be concluded that the most negative NBO (Natural Bond Orbital) charge in $[Nb_6O_{19}]^{8-}$ is -1.001 which is much higher than the NBO charge of WO_4^{2-} (the index of strong basicity which is -0.934 [53]) and other POMs. Moreover, the terminal oxygens possess more negative charge than bridging oxygens with in $[Nb_6O_{19}]^{8-}$, which can be regarded as the basic catalytic sites in the catalytic reaction.

2. Results and discussion

2.1. Basicity study

According to the literature, the basic active sites are located at the oxygen atom on the surface of POMs, and the higher negatively charged polyanions may possess stronger basicity [51]. Herein, the basicity of Nb_6 was investigated by NBO and compared with other three polyanions ($W_6O_{19}^{2-}$: W_6; $Nb_{10}O_{28}^{6-}$: Nb_{10}; $SiW_{12}O_{40}^{4-}$: SiW_{12}). As shown in Fig. 1a, the oxygen atoms charge in Nb_6 by NBO analysis are divided into five species corresponding to the values -0.809, -0.859, -0.869, -0.975, -1.001, where red rhombuses and blue circles represented the charge of terminal oxygens and bridging oxygens in Nb_6, respectively. Obviously, the terminal oxygens possess more negative charge than bridging oxygens with in Nb_6, which is different from Nb_{10} but the same to $SiNb_{12}O_{40}^{16-}$ ($SiNb_{12}$) [51,53]. Additionally, there is the comparison of the most negative charge among Nb_6 and three above polyanions in Fig. 1b, where the data spots presented the most negative charge in these compounds. The results showed that the most negative charge of Nb_6 is much higher than those of $W_6O_{19}^{2-}$ (-0.719), $Nb_{10}O_{28}^{6-}$ (-0.884), SiW_{12}^{4-} (-0.750). It must be mentioned that the NBO charges of oxygen atoms in Nb_6 are even more negative than the one (-0.934) in WO_4^{2-}, which imply that the superior basicity of Nb_6 is likely to be used as the base catalyst.

2.2. Catalysis

Considering the splendid basicity of Nb_6 has, it was employed as a base catalyst for Knoevenagel condensation reaction. Initially, the condensation reaction of benzaldehyde with ethyl cyanoacetate was carried out with different catalysts. The results of parallel experiments have been presented in Table 1, which have shown that there was little reactivity of this transformation in the absence of catalyst (entry 1). However, there was a great improvement in yield of product with NaOH loading in this system (entry 2), which has implied that the process benefited from basicity. Therefore, the lacunary POTs (entries 5, 7,11, 12) are more active than the plenary ones (entries 8, 9, 10, 13). In addition, precursors of Nb_6 (Nb_2O_5, $Nb_2O_5\cdot xH_2O$) have no obvious activity for the reaction. Strikingly, Nb_6 has exhibited the best catalytic performance for the reaction at the same conditions, which is in good consistent with its splendid basicity.

2.3. Influence of different factors on the process

To our best knowledge, reaction temperature, dosage of catalyst, raw ratio and solvents all play critical roles in this process, which were investigated in detail via the condensation reaction of benzaldehyde with ethyl cyanoacetate as the model reaction catalyzed by Nb_6 in various conditions. As shown in Fig. 2a, when 0.1 mol% catalyst was employed, 91% of yield for the reaction could be obtained. Moreover, the increase of yield would continue by the addition of the mass loading. Obviously, more catalytic dosage would improve the reaction rate. As to the effect of temperature, the results of condensation of benzaldehyde with ethyl cyanoacetate were studied at different temperatures shown in Fig. 2b. From 25 °C to 40 °C, there is a remarkable improvement in the yield of product. With the increase of temperature going on from 40 °C to 60 °C, there is also an enhancement of product and when the temperature comes to 60 °C, the highest yield of product was obtained corresponding to the yield of 98%. Considering the effect of raw ratio, the results of 0.6: 1, 0.8:1, 1:1 and 1.2:1 (donor: acceptor) have been presented in Fig. 2c, which showed that any ratio could be quicker to reach the limitation of the reaction than expected 1:1. Given that solvents also have an effect on this reaction, consequently, several contrast experiments were performed in various solvents. As the results shown in Fig. 2d, the catalyst in C_2H_5OH has the best performance for the process where an excellent yield of 98% has been obtained. Meanwhile, Nb_6 also exhibited good yield although the reaction took place in various solvents, which suggested that Nb_6 could be regarded as a wonderful catalyst for processing the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

2.4. Kinetic study

In order to obtain the kinetic parameters of the reaction, several catalytic experiments were performed by mixing catalyst, benzaldehyde and ethyl cyanoacetate in ethanol at different times and temperatures. Fig. 3a–d are the plots obtained for the yield of product and $C/[C_0(C_0-C)]$ as the function of reaction time, where C is the corresponding concentration of benzaldehyde transformed to product at time t and initial concentration of benzaldehyde is C_0. As indicated by stars in Fig. 3a–d, they fall into the quasi-linear plot of reaction time and $C/[C_0(C_0-C)]$, which reveals that the reaction catalyzed by Nb_6 exhibits second-order kinetics for the Knoevenagel condensation. The different rate constants (k_1, k_2, k_3, k_4) were determined at corresponding temperature (25 °C, 40 °C, 50 °C, 60 °C, respectively) according to Eqs. (1) and (2), which have been calculated as follows: $k_1 = 0.03551$ $(mol/L)^{-1}(min)^{-1}$, $k_2 = 0.08954$ $(mol/L)^{-1}(min)^{-1}$, $k_3 = 0.14981$ (mol/