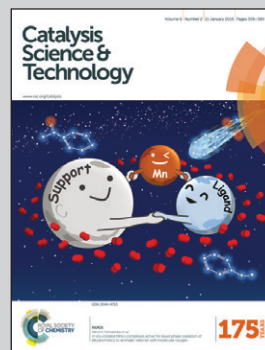


Showcasing research from Prof. Jun Wang's group at the College of Chemical Engineering, Nanjing Tech University, China.

Title: Fully-occupied Keggin type polyoxometalate as solid base for catalyzing CO_2 cycloaddition and Knoevenagel condensation

The good basicity of highly charged polyoxometalate $\text{Na}_{16}[\text{SiNb}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ was demonstrated by both density functional theory (DFT) calculations and experimental characterizations. This is the first report of intrinsic basicity in numerous fully-occupied Keggin polyoxometalates. It shows efficient and stable activities in catalyzing CO_2 cycloaddition and Knoevenagel condensation reactions.

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6, 460Fully-occupied Keggin type polyoxometalate as
solid base for catalyzing CO₂ cycloaddition and
Knoevenagel condensation†

Weilin Ge, Xiaochen Wang, Lingyu Zhang, Lei Du, Yu Zhou* and Jun Wang*

The highly negatively charged alkaline Keggin type polyoxometalate (POM) Na₁₆[SiNb₁₂O₄₀]·xH₂O (NaSiNb₁₂) was synthesized and used as an efficient solid base catalyst for CO₂ cycloaddition and Knoevenagel condensation reactions. This is the first report of the basicity of a fully-occupied POM with the Keggin type structure. Theoretical calculations by the density functional theory (DFT) method revealed the high negative NBO (natural bond orbital) charges (−0.919–1.029) of the oxygen atoms in [SiNb₁₂O₄₀]^{16−}, suggesting the existence of basicity, which was confirmed by CO₂-TPD and the *in situ* FT-IR spectra of methanol absorbed on the POM solid. Catalysis tests indicated that the POM solid base was very efficient in catalyzing the heterogeneous Knoevenagel condensation, giving high conversion and selectivity for several substrates. The catalyst NaSiNb₁₂ also presented high activity in the cycloaddition of CO₂ to epichlorohydrin under relatively mild conditions (120 °C, 1 MPa) in the absence of any solvent or co-catalyst. This solid base catalyst could be reused five times without an obvious decrease in the conversion and selectivity.

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Introduction

Polyoxometalates (POMs) are composed of an interior central heteroatom XO₄ tetrahedral cluster (X = P, Si, Ce, *etc.*), and corner-sharing and edge-sharing transition metal MO₆ octahedra clusters (M = Mo, V, Nb, W, Fe, *etc.*).¹ Due to the variety of synthetic parameters, the composition and characteristic of POMs are highly tunable. For example, the charge, solubility and geometry of POMs can be varied by adjusting the metals or counter ions. Therefore, POMs have attracted much attention in broad research fields such as in medicine, electron and catalytic science.^{2–6} Up to now, a lot of POM catalysts have been developed and used in acid and oxidative reactions because of their superior oxidative potential, electron-transfer ability and tunable acidities. Various modified POMs have been reported to be efficient homogeneous or heterogeneous catalysts for conventional organic reactions such as esterification,⁷ transesterification,⁸ Friedel–Crafts alkylation,⁹ benzene oxidation,¹⁰ alcohol oxidation¹¹ and alkene epoxidation.¹²

Nevertheless, POM derived basic catalysts are scarcely investigated because most POMs only present weak basic

properties. The modification of POM anions with basic organic cations can improve the basicity of POM compounds but the basic sites are located in the cations. Recently, negatively charged lacunary POMs are proved to possess basicity in the POM anions. For example, Mizuno and co-workers reported that some di-lacunary POMs with a highly negative charge acted as efficient basic catalysts for Knoevenagel condensation¹³ and acylation.¹⁴ Song *et al.* developed highly charged tri-lacunary POM catalysts for cyanosilylation and Knoevenagel condensation.¹⁵ Besides, Mizuno also revealed the basicity of simple monomeric tungstate TBA₂[WO₄] and applied it as an efficient basic catalyst in the chemical fixation of CO₂.^{16,17} The basicity of [WO₄]^{2−} was proved to arise from the high charge density calculated by density functional theory (DFT). These studies indicated that the basic strength of POM anions increased with the negative charges of the oxygen atoms in the POM. All those previously reported basic POMs were lacunary Keggin type; yet, no fully-occupied POM with full Keggin structure has been reported to possess superior basicity.

The Knoevenagel condensation of carbonyl compounds with active methylene compounds is one of the most important and classic C–C bond forming reactions.¹⁸ It is widely employed in producing important intermediates in chemical industries like perfume and medicine.¹⁹ Various homogeneous and heterogeneous catalytic systems have been developed for this reaction.^{14,15,20–29} Lacunary and organic-modified plenary Keggin type POMs^{20,21} can efficiently catalyze Knoevenagel

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condensation reactions. However, to the best of our knowledge, no fully-occupied POM with inorganic counter cations appears to be an efficient catalyst for Knoevenagel condensation.

On the other hand, with the increased CO₂ content around our atmosphere, “global warming” has become more and more severe.³⁰ Hence, the utilization and transformation of CO₂ to fine chemicals has been one of the top current interests.³¹ CO₂ cycloaddition with epoxides to produce the important chemical products of carbonates, which are widely used in the polymer industry, as electrolytes and in the pharmaceutical industry, is recognized as one of the most promising routes for the conversion of CO₂.³² In the past decades, great efforts have been devoted to developing efficient catalytic systems for CO₂ fixation.^{33–39} POMs modified with N-containing organic cations were efficient in CO₂ conversion;^{33–36} however, neat inorganic POM compounds are rarely found to be active in CO₂ cycloaddition.

In this work, we report for the first time the superior basicity of the highly negatively charged fully-occupied Keggin type POM compound Na₁₆[SiNb₁₂O₄₀] \cdot xH₂O (denoted as NaSiNb₁₂). Nyman *et al.* has successfully synthesized the single crystal of dodecaniobate Keggin type NaSiNb₁₂.⁴⁰ Despite this early finding in the field of POM synthesis, no basicity study of NaSiNb₁₂ has been performed before. Here, theoretical calculations are used to investigate the potential basicity of NaSiNb₁₂. Analyses of the temperature program desorption of carbon dioxide (CO₂-TPD) and *in situ* methanol absorption FT-IR spectra are also conducted to further illustrate the basicity of this kind of plenary Keggin POM. The catalytic performances of NaSiNb₁₂ are assessed in Knoevenagel condensation and CO₂ cycloaddition reactions. For comparison, two control samples of the common Keggin POM salt Na₃PW₁₂O₄₀ and monomeric tungstate Na₂WO₄ are used in the studies of basicity and catalysis.

Experimental section

Materials and methods

All the chemicals (solvents and reagents) were of analytical grade and used as received. X-ray diffraction (XRD) measurements were made with a SmartLab diffractometer (Rigaku Corporation) equipped with a 9 kW rotating anode Cu source at 40 kV and 100 mA, from 5 to 60° with a scan rate of 0.2° s⁻¹. The morphology and the elemental distribution were studied by a field emission scanning electron microscope (FESEM; Hitachi S-4800, accelerated voltage: 5 kV) accompanied by Energy dispersive X-ray spectrometry (EDS; accelerated voltage: 20 kV). The metallic content was investigated further by X-ray Fluorescence (XRF, Rigaku ZSX PrimusII) with Rh end-window tube and SQX calculation software. Transmission electron microscopy (TEM) analysis was performed on a JEM-2100 (JEOL) electron microscope operating at 200 kV. The surface areas were measured at the temperature of liquid nitrogen (77 K) by using a BELSORP-MINI analyzer, and the samples were degassed at 150 °C for 3 h before analysis. Thermo gravimetry (TG) analysis was carried

out with a STA409 instrument in dry air at a heating rate of 10 °C min⁻¹. *In situ* FT-IR spectra were recorded on an Agilent Cary 660 FT-IR instrument with 64 scans. The spectra were presented after subtraction of the background before the admission of methanol to the infrared cell. Carbon dioxide temperature program desorption curves (CO₂-TPD) were recorded on a BELCAT-B temperature programming unit equipped with a thermal conductivity detector (TCD). In a typical run, a 0.1 g sample was placed in a U-shaped quartz cell and preconditioned at 300 °C in He gas for 2 h, followed by cooling down to 100 °C in He flow. Then, the sample was saturated with CO₂ at 100 °C for 45 min. After that, the sample was exposed to He for the removal of the physically adsorbed CO₂. Subsequently, the TPD profile was recorded upon heating the sample at a rate of 10 °C min⁻¹ up to 325 °C.

Catalyst preparation

The synthesis of Na₁₆SiNb₁₂O₄₀ involved two main steps. The first step was the synthesis of the precursor Nb₂O₅ \cdot xH₂O, according to the previous literature.⁴¹ In a typical procedure, commercial Nb₂O₅ (6.14 g, 0.024 mol), NH₄HF₂ (3.12 g, 0.054 mol) and H₂O (12.48 g, 0.693 mol) were mixed in a 50 mL Teflon-lined autoclave and kept at 180 °C for 24 h. After cooling to room temperature, the solid was separated by filtration, washed with H₂O and dried, giving a white solid. The second step was the synthesis of Na₁₆SiNb₁₂O₄₀ using the above pre-prepared Nb source. According to the previous literature,⁴⁰ 0.35 g of the prepared Nb₂O₅ \cdot xH₂O, 0.26 g sodium hydroxide (NaOH) and 0.27 g tetraethylorthosilicate (TEOS) were dissolved in 8 g of H₂O in a 25 mL Teflon-lined autoclave. After stirring for 30 min, the autoclave was sealed and kept at 190 °C for 48 h. After that, the white solid was separated by filtration, washed until neutral with ethanol, and dried overnight in a 100 °C vacuum oven. The resulting solid was denoted as NaSiNb₁₂. During the synthesis, the initial amount of the precursor Nb₂O₅ \cdot xH₂O, the stirring time, crystallization temperature and reaction time were optimized by varying one parameter while keeping the others unchanged.

Catalytic test

The catalytic activities of NaSiNb₁₂ and the other control catalysts were tested in two kinds of reactions: 1) the Knoevenagel condensation of various carbonyl compounds with active methylene compounds, and 2) CO₂ cycloaddition with epoxide.

In a typical run of the Knoevenagel condensation, 10 mmol aldehyde, 10 mmol of a methylene compound, and 2 mL CH₃OH were mixed in a 25 mL round-bottomed flask reactor equipped with a condenser under a nitrogen atmosphere. A calculated amount of the catalyst (0.05 g) was added into the mixture and the reaction slurry was stirred at 70 °C for 2 h. After the reaction, the internal standard *n*-dodecane was added to the resulting mixture, and then the solution was diluted with ethanol. The reaction mixture was centrifuged to remove the solid catalyst, and the liquid was

analyzed by gas chromatography (Agilent GC 7890B) equipped with a FID detector and a capillary column (HP-5, 30 m \times 25 mm \times 0.25 μ m). The hot filtration test for removal of the solid catalyst was conducted at 0.5 h, with the filtrate being further reacted.

In a typical CO₂ cycloaddition experiment, 5 mmol epichlorohydrin and 0.1 g of catalyst were placed in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer. After being carefully flushed with CO₂, the autoclave was sealed. The reaction was carried out at a specified temperature and CO₂ pressure for a desired period of time. After the reaction, the reactor was cooled in an ice-water bath and slowly depressurized. The internal standard *n*-dodecane (0.5 g) was added and the resulting mixture was diluted with ethyl acetate. The reaction mixture was centrifuged to remove the solid catalyst, and the liquid was analyzed by gas chromatography (Agilent 7890B) equipped with a FID detector and a capillary column (HP-5, 30 m \times 0.25 mm \times 0.25 μ m). Gas chromatography-mass spectrometry (GC-MS, Bruker Scion 436) was also used to confirm the composition of cycloaddition products. The catalyst was recovered by centrifugation, washed with hot ethanol three times, and dried under vacuum. The catalyst reusability was tested in a five-run cycling experiment.

Quantum chemical calculations

The calculations were carried out by using Gaussian 09 programs at the B3LYP level of theory with 6-31++G* basis sets for H and O atoms and the double-quality basis sets with effective core potentials proposed by Hay and Wadt for Nb and W atoms.

Results and discussion

Materials synthesis

According to a previous report,⁴⁰ the highly negatively charged fully-occupied Keggin-structured POM Na₁₆[SiNb₁₂O₄₀] is synthesized by a hydrothermal reaction between Nb₂O₅·*x*H₂O, NaOH, TEOS and H₂O. We observe that various synthetic parameters significantly influence the crystallinity of the obtained sample; therefore, the molar composition of the precursors, the stirring time, and the crystallization temperature and time were systematically investigated. After optimization, the suitable synthetic parameters were found to be as follows: 0.35 g Nb₂O₅·*x*H₂O, 0.26 g NaOH, 0.27 g TEOS and 8 g H₂O are mixed and stirred for 30 min, and then hydrothermal crystallization is conducted at 190 °C for 48 h.

Fig. 1A shows the XRD pattern of the thus obtained solid product. The well defined crystal diffraction peaks similar to those previously reported⁴⁰ indicate that the synthesized product is the Keggin POM Na₁₆[SiNb₁₂O₄₀]·*x*H₂O (shortened to NaSiNb₁₂). The morphology of NaSiNb₁₂ is characterized by the SEM images in Fig. 1B. The primary crystals of NaSiNb₁₂ are loosely packed rod-like fibers with lengths of more than 3 μ m and widths of about 40 nm (Fig. 1B). The NaSiNb₁₂ sample is further examined by high resolution

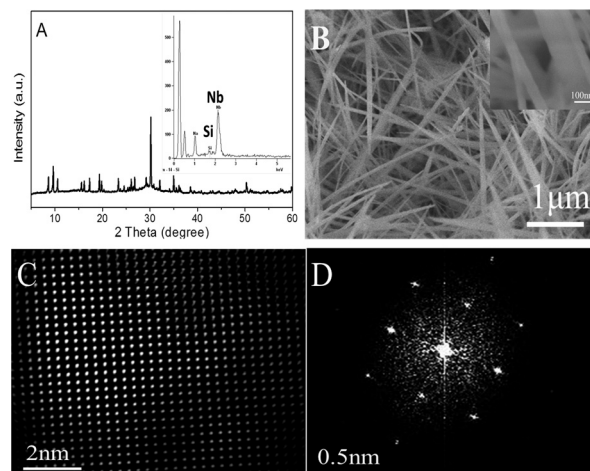


Fig. 1 (A) The XRD pattern (inset: selected energy dispersed X-ray spectrum), (B) SEM images, (C) TEM inverse FFT image and (D) simultaneously recorded selected-area electron diffraction pattern of NaSiNb₁₂.

transmission electron microscopy (HR-TEM) images (Fig. 1C and D). The well-defined and clear lattice fringes observed in the inverse FFT TEM image (Fig. 1C), together with the selected-area electron diffraction pattern (Fig. 1D), confirms that the NaSiNb₁₂ material in this work has good crystallinity with a pure structure. Elemental mapping images of NaSiNb₁₂ (Fig. S1†) reveal the uniform dispersion of Si, Nb and O element throughout the primary particle. EDX analysis (inset of Fig. 1A) gives a Nb/Si molar ratio of 11.7 that is close to the theoretical value of 12, but as it is difficult to accurately measure a light element like Na using EDX, the data shows a lower Na/Si molar ratio of 13.0 compared to the theoretical value of 16. Further measurement by XRF shows the Na/Si molar ratio to be 18, which is slightly higher than the calculated value. Thus other than the above XRD and TEM results, the EDX and XRF data complementarily support the successful synthesis of the target POM Na₁₆[SiNb₁₂O₄₀]·*x*H₂O.

The nitrogen adsorption-desorption isotherm of NaSiNb₁₂ is type IV with a H1-type hysteresis loop at a relatively low partial pressure region of $P/P_0 = 0.3-0.99$ (Fig. 2), implying the existence of mesopores in NaSiNb₁₂. The inset of Fig. 2 is the pore size distribution curve of NaSiNb₁₂, which exhibits a relatively narrow pore size distribution with an average pore diameter of *ca.* 14.6 nm. As a result, NaSiNb₁₂ has a moderate BET surface area of 38 m² g⁻¹ and a pore volume of 0.14 cm³ g⁻¹. TG analysis indicates that the obtained NaSiNb₁₂ exhibits relatively high thermal stability in air (Fig. S2†). According to the TG results, the crystalline water per POM unit (*x*) is around 4, which is close to that in a previous report.⁴⁰

Basicity study

The basicity of NaSiNb₁₂ is investigated and compared with two control samples (Na₃PW₁₂O₄₀ and Na₂WO₄). Normally, the acidic forms of fully-occupied Keggin-type POMs such as

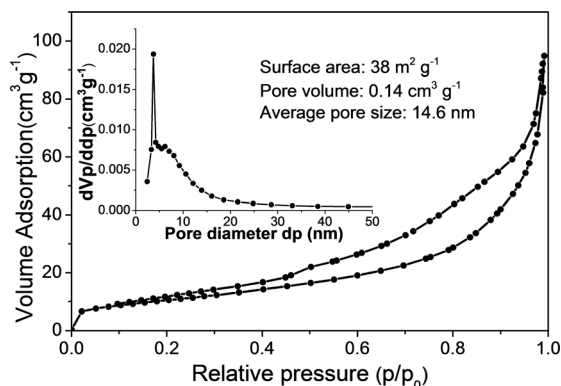


Fig. 2 N_2 sorption isotherm and pore size distribution curve (inset) of NaSiNb_{12} .

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ are strong acids, while their sodium forms such as $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ are very weak bases and cannot be used as basic catalysts. In contrast, the highly negatively charged oxygens in the POM-anions can act as Lewis base sites and various di- and tri-lacunary POMs were developed as good candidates for basic catalysis.^{13–15} Besides, the monomeric tungstate anion $[\text{WO}_4]^{2-}$ was also found to possess basic properties and presented good catalytic performance in some basic reactions.^{16,17}

Previous works indicate that 1) the deprotonated oxygen atoms in monomeric tungstate and lacunary Keggin-type POMs can work as structurally well-defined active sites for basic reactions;¹³ 2) the basicity of an oxygen atom in POM anion can be strongly affected by the charge of the POM and the basicity increases with an increase in its negative charge density.¹⁶ In other words, the negative charges of the oxygen atoms in the POM anions are closely related to the basicity of the POM. In order to study the basicity of NaSiNb_{12} , theoretical calculations are performed. The energies of NaSiNb_{12} and $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ are calculated by a density functional theory (DFT) method. Fig. 3 shows the calculated molecular structures and NBO (natural bond orbital that features the formulation in terms of natural atomic orbitals (NAOs), a complete orthonormal set for optimally describing the effective atom-like constituents within a molecular environment⁴²) charges of oxygen atoms in $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$, $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and $[\text{WO}_4]^{2-}$. The oxygen atom in $[\text{WO}_4]^{2-}$ has a NBO charge of -0.934 , an index of high basicity.¹⁶ The single-crystal data of NaSiNb_{12} revealed two crystallographically distinct $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ α -Keggin ions in the unit cell.¹⁸ Both of the two anions present much lower NBO charges of the oxygen atoms, ranging from -0.919 to -1.029 (Fig. 3A). The above values are much lower than those (-0.528 – -0.704 , Fig. 3B) in $\text{PW}_{12}\text{O}_{40}^{3-}$, which is also a fully-occupied Keggin structure. Comparison of the results strongly suggests the existence of basicity on the $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ anions. In addition, the NBO charges (-0.999 – -1.029) of the oxygen atoms in Keggin 2 $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ are even more negative than the one (-0.934) in $[\text{WO}_4]^{2-}$, suggesting the superior basicity of the former compared to the latter.

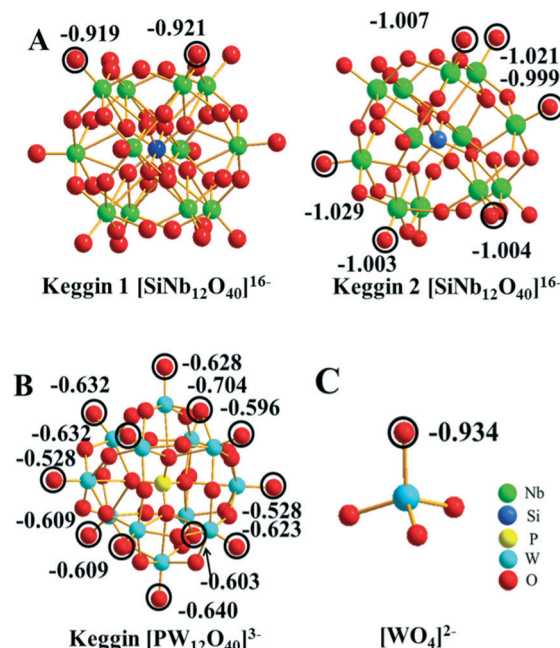


Fig. 3 Calculated molecular structures and NBO charges of oxygen atoms in (A) $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$, (B) $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and (C) $[\text{WO}_4]^{2-}$. The NBO charge of $[\text{WO}_4]^{2-}$ is cited from ref. 16.

CO_2 -TPD analysis is frequently used in the investigation of the basicity of solid materials. Fig. 4 depicts the CO_2 -TPD curves of $\text{Na}_3\text{PW}_{12}\text{O}_{40}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NaSiNb_{12} . Only a very small desorption peak is observed over $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ due to its weak basicity (curve c). The area of the desorption peak increases over $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (curve b), indicating enhanced basicity. A clear desorption peak is detected over NaSiNb_{12} and its area is larger than the one over $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, suggesting the superior basicity of NaSiNb_{12} (curve a). In addition, the CO_2 pre-adsorption treatment during this CO_2 -TPD analysis proceeded at 100°C and the maximum desorption temperature is centered at 180 – 190°C , which is indicative of the medium (rather than weak) basic strength of NaSiNb_{12} .⁴³

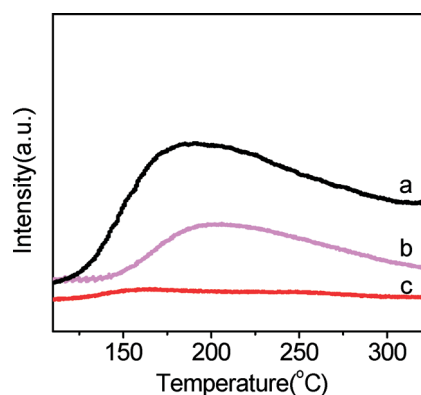


Fig. 4 CO_2 -TPD curve of methanol adsorbed on (a) NaSiNb_{12} , (b) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and (c) $\text{Na}_3\text{PW}_{12}\text{O}_{40}$.

The basicity of NaSiNb_{12} is further characterized by *in situ* FT-IR methanol absorption spectroscopy. Fig. 5 shows the spectra of methanol adsorbed on $\text{Na}_3\text{PW}_{12}\text{O}_{40}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NaSiNb_{12} at 200 °C. Normally, methanol can be adsorbed through 1) interaction between the metal cation (electron pair acceptor) and the oxygen of methanol (electron pair donor), or 2) interaction of the hydrogen atoms of methanol to the negatively charged oxygen atoms in metal oxides. The interaction between the adsorbate and adsorbent will be enhanced with an increase in negative charge in the oxygen atoms of the adsorbents.⁴⁴ In this work, the less negatively charged oxygen atoms in $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ provide an insufficient interaction with methanol, therefore a weak signal is detected over $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ (curve a), which suggests that only a trace amount of methanol can be adsorbed under these conditions. On the contrary, the highly negatively charged oxygen atoms in $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NaSiNb_{12} strengthen the interactions with methanol. Both the spectra of the methanol adsorbed $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NaSiNb_{12} exhibit characteristic peaks of C–H vibrations in the region of 3100–2800 cm^{-1} (curves b and c). The signals at 2949 and 2836 cm^{-1} correspond to the $\nu_{\text{as}}(-\text{CH}_3)$ and $\nu_{\text{s}}(-\text{CH}_3)$ stretching vibrations of the adsorbed methanol molecule.⁴⁵ The band at about 2921 cm^{-1} is caused by an overtone of the bending mode of $-\text{CH}_3$. The emergence of these peaks indicates the adsorption of methanol over $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NaSiNb_{12} . A stronger peak intensity is observed over NaSiNb_{12} than over $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, suggesting an enhanced interaction between NaSiNb_{12} and methanol, which is due to the more highly negatively charged oxygen atoms in Keggin 2 $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$, demonstrated by the DFT calculations.

Catalytic activity in Knoevenagel condensation

The catalytic performance of NaSiNb_{12} in a basic reaction is investigated in the Knoevenagel condensation, which is one of the most significant reactions for the formation of C–C bonds. Table 1 compares the activities of various catalysts in

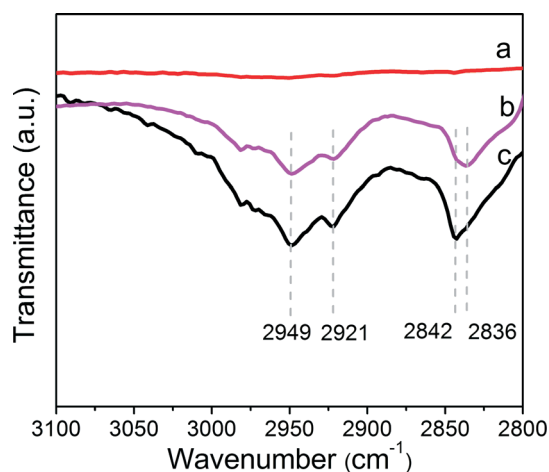
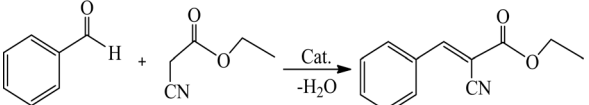


Fig. 5 *In situ* FT-IR spectra of methanol adsorbed on (a) $\text{Na}_3\text{PW}_{12}\text{O}_{40}$, (b) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and (c) NaSiNb_{12} .

the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate under solvent-free conditions. The conversion is 5.9% in the absence of any catalysts (entry 1), while the lead catalyst NaSiNb_{12} exhibits a conversion of ethyl cyanoacetate 66.7% with perfect selectivity of 100% towards the target product (entry 2). For comparison, various precursors of NaSiNb_{12} were tested under the same conditions. The commercial Nb_2O_5 offers a conversion of 6.2% (entry 4), which is at a similarly low level to our prepared precursor $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (7.1%, entry 5). When another precursor SiO_2 is used, the low conversion of 6.4% is detected (entry 6). Obviously, relative to NaSiNb_{12} , all the precursor samples present much lower catalytic activities in this reaction. Several other commercial tungstates were similarly tested. The well-known Si-containing heteropolyacid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ gives a low conversion of 14.2% (entry 7) due to its lack of basicity. Also, the sodium form Keggin-type POM $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ displays a low conversion of 23.3% due to its weak basicity as mentioned above (entry 8). If Na_2WO_4 is added to the reaction system, the conversion is 52.5% (entry 9), which is higher than the system containing solely $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ because of the increased basicity. However, the conversion over Na_2WO_4 is still lower than that with NaSiNb_{12} . The reason can be assigned to the further increased basicity of NaSiNb_{12} , in accordance with the above basicity studies.

The basic activity of NaSiNb_{12} is further investigated in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate by using different organic solvents. As demonstrated in Fig. S3A,† when acetonitrile and toluene are used as the solvent, the conversions are 22.8% and 54.5% respectively, which are even lower than that for the conversion without any solvents. By contrast, if ethanol or methanol are used, the conversion of ethyl cyanoacetate greatly rises to 89.2% and 91.1%, respectively. Previous work has indicated that a protic polar solvent can help to activate the substrate; therefore, methanol or ethanol solvents have the ability to improve the catalytic activity due to the O–H interaction.^{21,46} Successively, the catalytic performance of NaSiNb_{12} using methanol as the solvent is optimized by systematically investigating the influence of various reaction parameters including the catalyst amount, reaction temperature and time (Fig. S3B–D†). NaSiNb_{12} is insoluble in methanol, and hence acts as a heterogeneous catalyst for this reaction. Hot filtration is carried out to remove the solid catalyst at a reaction time of 0.5 h (conversion 76.5%). The reaction proceeds with the filtrate, giving a slightly increased yield of 4.8% at 2.5 h, close to the increase of the blank (5.9%), supporting the heterogeneity of NaSiNb_{12} in this reaction. A high conversion of 97.2% and a selectivity of 100% over NaSiNb_{12} can be achieved under the optimal reaction conditions: 10 mmol benzaldehyde, 10 mmol ethyl cyanoacetate, 2 mL methanol, 0.1 g catalyst (0.449 mol% to substrate), 2 h, 70 °C.

Moreover, the recycling catalytic performance of NaSiNb_{12} is investigated to measure the reusability of the catalyst. A five-run recycling test of NaSiNb_{12} was investigated under the above optimized reaction conditions and the results are

Table 1 Catalytic performances of various catalysts in Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate without solvent^a


Entry	Catalyst	Con ^b (%)	Sel ^c (%)	Yield ^d (%)
1	None	5.9	100	5.9
2	NaSiNb ₁₂	66.7	100	66.7
3	Nb ₂ O ₅ (commercial)	6.2	100	6.2
4	Nb ₂ O ₅ ·xH ₂ O	7.1	100	7.1
5	SiO ₂	6.4	100	6.4
6	H ₄ SiW ₁₂ O ₄₀	14.2	100	14.2
7	Na ₃ PW ₁₂ O ₄₀	23.3	100	23.2
8	Na ₃ WO ₄	52.5	100	52.5

^a Reaction conditions: catalyst 0.05 g, benzaldehyde 10 mmol, ethyl cyanoacetate 10 mmol, 70 °C, 2 h. ^b GC conversion based on ethyl cyanoacetate. ^c GC selectivity for target product ethyl (E)-a-cyanocinnamate. ^d GC yield.

shown in Fig. 6. A high conversion of 97.2% is achieved for the first run. By facile centrifugation, NaSiNb₁₂ can be directly reused in the next run without any activation treatment, giving conversions of 97.1, 96.9, 96.9 and 96.7% for next four runs with a high selectivity of 100% (Fig. 6). The result shows a small decrease in activity upon reuse of the catalyst, revealing that NbSiNb₁₂ is a robust and reusable catalytic material for the Knoevenagel condensation reaction.

The catalytic activities of the catalyst NaSiNb₁₂ towards several other substrates of carbonyl or methylene compounds are summarized in Table 2. When the methylene compound malononitrile is used to react with benzaldehyde in the solvent of methanol at room temperature of 25 °C, a high conversion of >99% is observed (entry 1). Moreover, the conversion remains at a high level of 98.5% even under solvent-free conditions with a much shorter reaction time of 0.5 h (entry 2). Previously, two basic POMs were tested in the Knoevenagel condensation of benzaldehyde and malononitrile.^{13,15} The homogeneous catalyst [γ-H₂GeW₁₀O₃₆]⁶⁻ gave a conversion of 99% under reaction conditions of benzaldehyde (1 mmol),

catalyst (1 mol% with respect to benzaldehyde), malononitrile (1.5 mmol), solvent (1 mL CH₃CN), 32 °C, 0.5 h.¹³ The yield over the heterogeneous catalyst Na₈H[A-PW₉O₃₄]-7H₂O (Na-A-PW₉) was 92% under reaction conditions of benzaldehyde (1 mmol), catalyst (0.25 mol% with respect to benzaldehyde), malononitrile (1.5 mmol), solvent (0.2 mL methanol), 25 °C, 6 h.¹⁵ The activity of the present catalyst NaSiNb₁₂, though with a much shorter reaction time and lower reaction temperature, is higher than that of Na-A-PW₉, and is comparable to [γ-H₂GeW₁₀O₃₆]⁶⁻. Notably, our catalyst NaSiNb₁₂ is tested under solvent-free conditions and with stoichiometric equimolar reactants (entry 2), whereas the previous basic POMs were evaluated in solvents of CH₃CN or methanol and with an excess amount of malononitrile.^{13,15} A similar comparison over the substrate of ethyl cyanoacetate (Table S1†) shows the conversion of 89.6% over NaSiNb₁₂, which is higher than the data of 80% over Na-A-PW₉, again revealing the good basic activity of NaSiNb₁₂ in the Knoevenagel condensation.

Further, NaSiNb₁₂ exhibits a conversion of 89.9% when catalyzing the condensation between ethyl cyanoacetate and 1-naphthaldehyde (Table 2, entry 3), which has a bigger molecular size than benzaldehyde. On the other hand, the conversion is 65.4% when the electron-donating hydroxyl-tethered aromatic aldehyde salicylaldehyde is used as carbonyl substrate, (entry 4). By contrast, the conversion is 90.9% (entry 5) when ethyl cyanoacetate reacts with the electron-withdrawing group (-Cl) attached aldehyde *p*-chlorobenzaldehyde. These results suggest a certain substrate compatibility of NaSiNb₁₂ for the Knoevenagel condensation.

Catalytic activity in CO₂ cycloaddition

Table 3 lists the catalytic behaviors of NaSiNb₁₂ and its control catalysts for CO₂ cycloaddition with epichlorohydrin in the absence of any solvents or other additives. Little target product is detected without a catalyst (yield <1%, entry 1). The catalyst NaSiNb₁₂ gives a conversion of 97.6% with a high selectivity of 98.9% (entry 2). Among the three precursor samples, only Nb₂O₅·xH₂O can convert the substrate to the target product cyclic carbonate, but with a low selectivity of 66.6%, though they all give conversions 70–80% (entries 3–5), while Nb₂O₅ and SiO₂ are almost inactive for yielding the desired cyclic carbonate. Similarly, the heteropolyacid H₄SiW₁₂O₄₀ shows a very high conversion of 100% but with only a trace amount of the cyclic carbonate product (entry 6). Na₃PW₁₂O₄₀, which has the same fully-occupied Keggin structure, demonstrates a conversion of 83.2% with a selectivity of 33% (entry 7), suggesting inferior activity due to its weak basicity. For Na₂WO₄, a conversion of 95.2% with a selectivity of 80% is achieved (entry 8). Clearly, the catalytic activity of Na₂WO₄ is better than that of Na₃PW₁₂O₄₀ due to the increased basicity of Na₂WO₄, but it is still inferior to that of NaSiNb₁₂, even if Na₂WO₄ has been proved to be effective in CO₂ fixation.¹⁶ This observation is exactly same as that in the Knoevenagel condensation, which can still be assigned to the mostly enhanced basicity of NaSiNb₁₂.

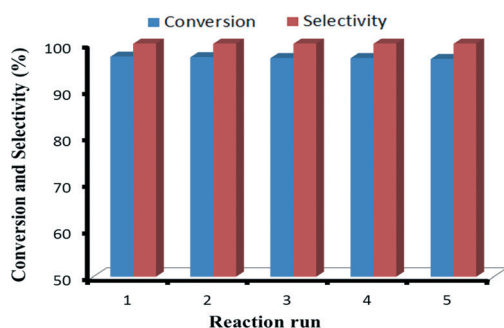


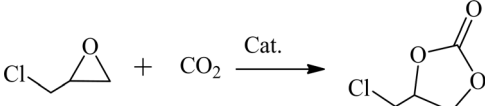
Fig. 6 Reusability of NaSiNb₁₂ in Knoevenagel condensation. Reaction conditions: benzaldehyde 10 mmol, ethyl cyanoacetate 10 mmol, 2 mL methanol, 0.1 g catalyst, 2 h, 70 °C.

Table 2 Knoevenagel condensation with various substrates catalyzed by NaSiNb₁₂^a

Entry	Substrate				Time (h)	Temperature (°C)	Conversion ^b (%)	Selectivity ^c (%)	Yield ^d (%)
	R ₁	R ₂	X	Y					
1	Ph	H	CN	CN	2	25	99.8	100	99.8
2 ^e	Ph	H	CN	CN	0.5	25	98.5	100	98.5
3	1-Naphth	H	CN	CO ₂ Et	2	70	89.9	100	89.9
4	2-OH-Ph	H	CN	CO ₂ Et	2	70	65.4	100	65.4
5	4-Cl-Ph	H	CN	CO ₂ Et	2	70	90.9	100	90.9

^a Reaction conditions: 0.05 g catalyst, aldehyde or ketone 10 mmol, methylene compound 10 mmol, 2 mL methanol. ^b GC conversion based on benzaldehyde for entry 1 and 2, GC conversion based on ethyl cyanoacetate for entry 3 and 4. ^c GC selectivity for target product ethyl (*E*)-α-cyanocinnamate. ^d GC yield. ^e Without solvent.

Table 3 Epichlorohydrin cycloaddition with CO₂ over different catalysts^a

				
Entry	Catalyst	Con ^b (%)	Sel ^c (%)	Yield ^d (%)
1	None	65.4	<1	<1
2	NaSiNb ₁₂	97.6	98.9	96.5
3	Nb ₂ O ₅ (commercial)	80.3	<1	<1 ^e
4	Nb ₂ O ₅ ·xH ₂ O	76.8	66.6	51.1
5	SiO ₂	70.7	<1	<1 ^e
6	H ₄ SiW ₁₂ O ₄₀	100	<1	<1 ^e
7	Na ₃ PW ₁₂ O ₄₀	83.2	33.5	27.9
8	Na ₂ WO ₄	95.2	80.5	76.6

^a Reaction conditions: 0.1 g catalyst, 5 mmol epichlorohydrin, CO₂ 1.0 MPa, 120 °C, 10 h. ^b GC conversion based on epichlorohydrin. ^c Selectivity based on GC results. ^d GC yield. ^e The majority of the by-product is polycarbonate and trace amount of by-product diols forms due to the existence of trace water.^{47,48}

In order to determine the catalytic stability of NaSiNb₁₂ in CO₂ cycloaddition, a five-run catalyst recycling test was performed, with the results shown in Fig. 7. The powder

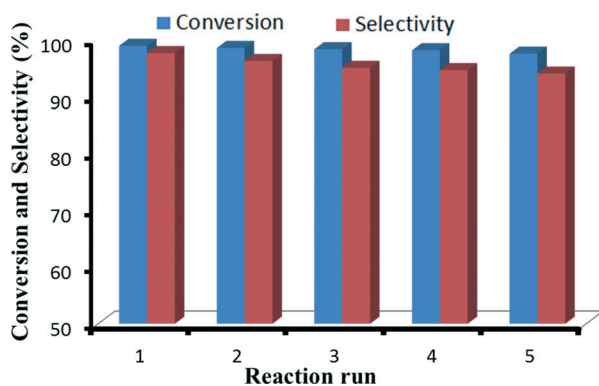


Fig. 7 Reusability of NaSiNb₁₂ in epichlorohydrin cycloaddition with CO₂. Reaction conditions: 0.1 g catalyst, 5 mmol epichlorohydrin, CO₂ 1.0 MPa, 120 °C, 10 h.

catalyst is recovered from a reacted liquid mixture and directly reused in the next run without adding fresh catalyst during the recycling test. The conversion of 97.6% and selectivity of 98.9% are observed for the first run, and the considerably high conversion of 94.1% and selectivity of 97.5% still remain for the 5th run, suggesting that the catalyst NaSiNb₁₂ can be steadily reused without a significant loss of activity.

The above result suggests that NaSiNb₁₂ can efficiently catalyze the conversion of CO₂ through the heterogeneous cycloaddition of CO₂ with epichlorohydrin. In early attempts, POM-catalyzed CO₂ cycloaddition usually occurred at a high temperature (*e.g.* 150 °C) and CO₂ pressure (*e.g.* 3 MPa), and sometimes, a certain solvent or co-catalyst was added; otherwise the activity became low.^{33–36} In contrast, we observe for the first time a high and stable activity of neat inorganic POM for heterogeneous CO₂ cycloaddition that is conducted at a relatively low temperature (120 °C) and CO₂ pressure (1 MPa) without being aided by any solvents or co-catalysts.

Conclusions

In summary, polyoxometalate Na₁₆[SiNb₁₂O₄₀]₂·xH₂O (NaSiNb₁₂) is proved to exhibit superior basicity due to the much lowered negative charge of the oxygen atoms of its Keggin-structured anion. This is the first time that considerable basicity of a neat fully-occupied Keggin type POM has been found. The obtained POM material NaSiNb₁₂ is insoluble in polar solution, and was demonstrated to be an efficient heterogeneous catalyst for Knoevenagel condensation and CO₂ cycloaddition under relatively mild conditions. This study provides some new insight into the design of basic POM catalysts.

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