

Supporting information

for

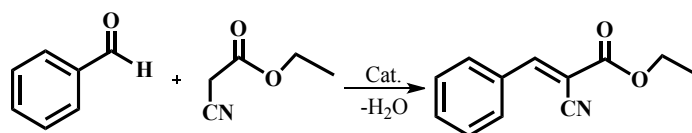
Fully-occupied Keggin type polyoxometalate as solid base for catalyzing CO₂ cycloaddition and Knoevenagel condensation

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Table S1. Catalytic performances of different catalysts in Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate.^a



Entry	Catalyst	Time(h)	Yield(%)
1	NaSiNb ₁₂	2	59.3
2	NaSiNb ₁₂	6	89.6
3 ^b	Na-A-PW ₉	6	80

[a] Reaction conditions: catalyst (0.25 mol% to benzaldehyde), benzaldehyde 10mmol, ethyl cyanoacetate 10mmol, 25 °C, 2mL ethanol. [b] The result is cited from the Ref. 15, reaction conditions: benzaldehyde (1 mmol), Na-A-PW₉ (0.25 mol% to benzaldehyde), ethyl cyanoacetate (1.5 mmol), 0.2 mL methanol, 25 °C, 6 h.

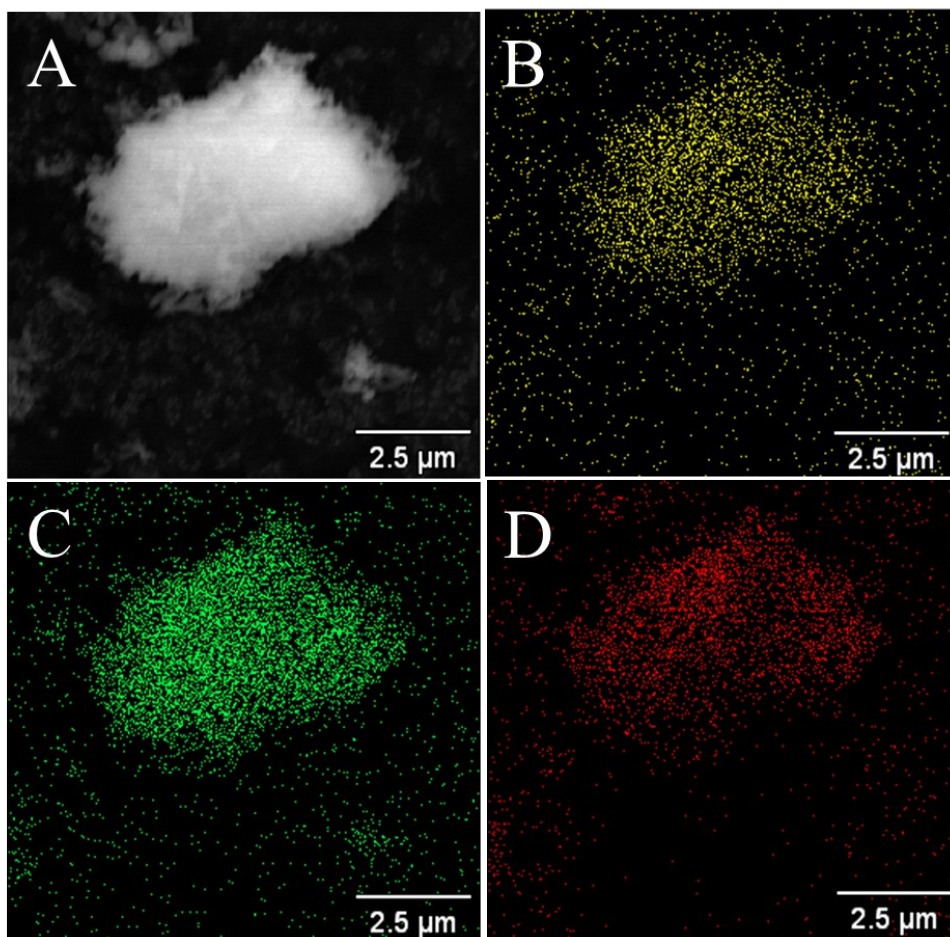


Figure S1 SEM (A) and elemental mapping images of (B) Si, (C) Nb and (D) O element for NaSiNb_{12} .

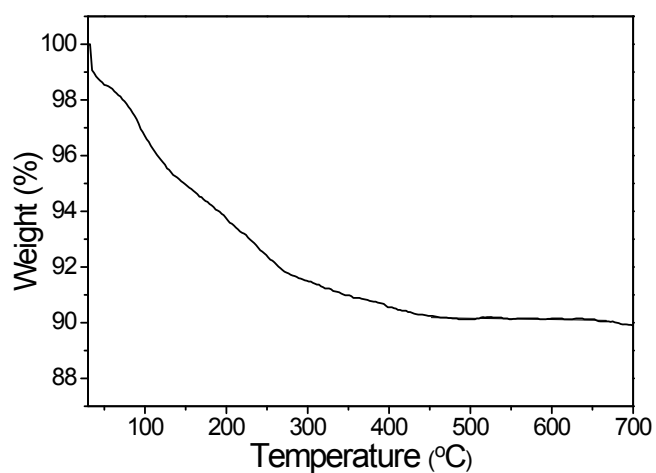


Figure S2 TG curve of NaSiNb_{12} . The weight loss below 200 °C was due to desorption of adsorbed water. In the next temperature range 200-450 °C, the weight loss is attributable to the loss of the crystalline water molecular and the 3.16% weight loss in this temperature range is close to the calculated one (3.32%) by assuming that one POM unit possessed four crystalline water molecular. Nevertheless, the synthesized NaSiNb_{12} of this work was not in single-crystal form, and it is hard to exactly determine the crystalline water by TG. Therefore, the formula of NaSiNb_{12} may be $\text{Na}_{16}[\text{SiNb}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ ($x \approx 4-5$).

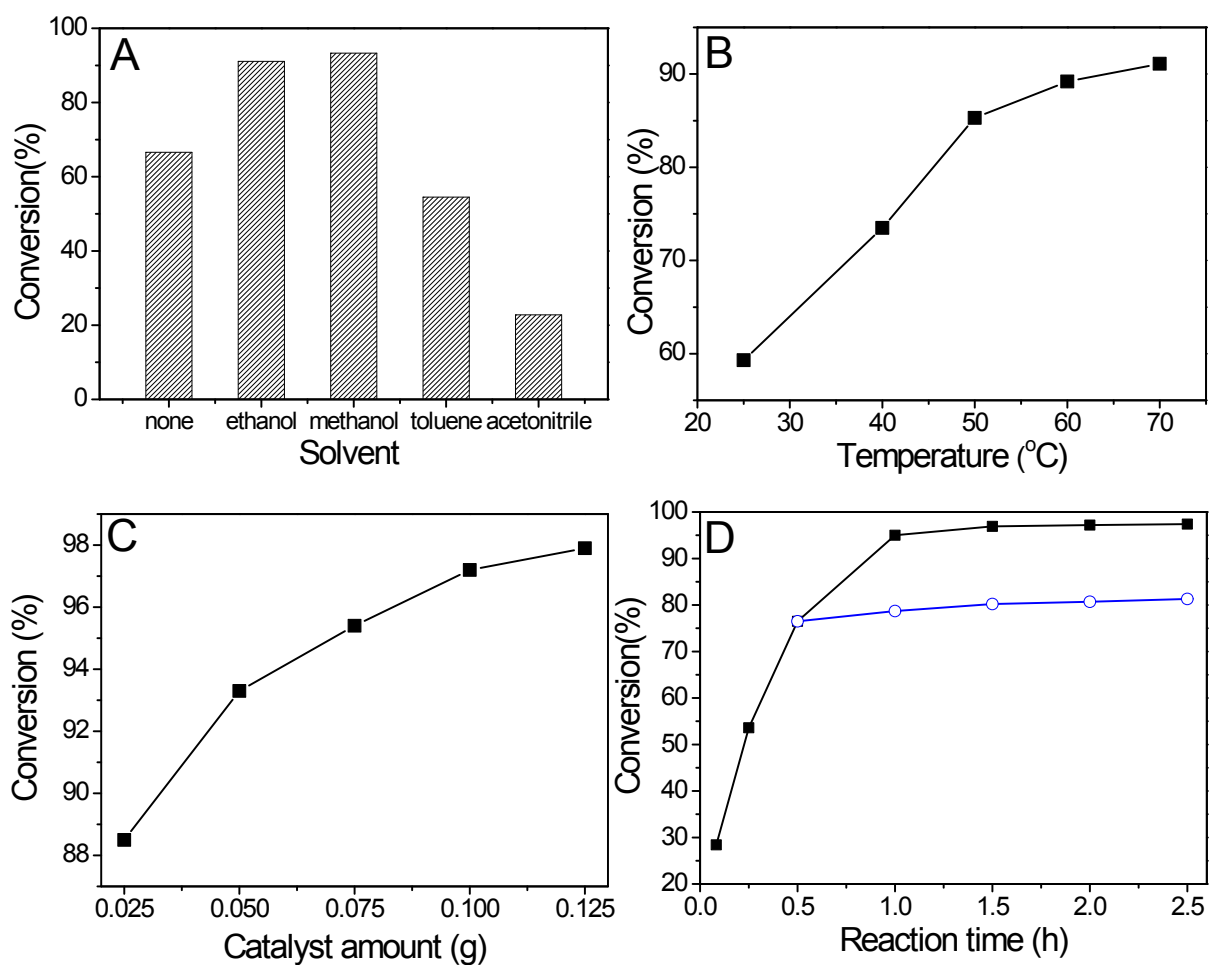


Figure S3 (A) The effect of solvent on the conversion over NaSiNb_{12} . Reaction conditions: 0.05 g catalyst, 2 mL solvent (if needed), 2 h, 343 K. (B) The effect of temperature on the conversion over NaSiNb_{12} . Reaction conditions: 0.05 g catalyst, 2 mL ethanol, 2 h, 343 K. (C) The effect of catalyst amount on the conversion over NaSiNb_{12} . Reaction conditions: 2 mL methanol, 2 h, 343 K. (D) The effect of reaction time on the conversion over NaSiNb_{12} (The reaction results in blue line after 0.5 h was conducted with catalyst removed). Reaction conditions: 0.1 g catalyst, 2 mL methanol, 343 K. All reactions are done with 10 mmol benzaldehyde and 10 mmol ethyl cyanoacetate.