Mesoporous Silica with Site-Isolated Amine and Phosphotungstic Acid Groups: A Solid Catalyst with Tunable Antagonistic Functions for One-Pot Tandem Reactions


One-Pot Tandem Reactions with a Bifunctional Solid Catalyst

Preparation of mesoporous silica catalyst 3:

1. \((\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2\) in PhMe, 110 °C, 24 h
2. \(\text{H}_3\text{PW}_{12}\text{O}_{40}\) in MeOH, 25 °C, 12 h

Reaction pathway:

Selected results:

4 (1 mmol) 3 (30 mg) HNO\text{$_3$} (10 mL) 50 °C, 12 h
4 (1 mmol) H$_2$O

5. tandem decacetalization–Henry reaction
98% conversion, 92% isolated yield

6. tandem decacetalization–Knoevenagel reaction
>98% conversion, 91% isolated yield

Significance: A mesoporous silica catalyst 3 bearing both Bronsted base and acid groups was prepared by immobilization of 3-amino propyltriethoxysilane \([\text{EtO}]_3\text{Si}(\text{CH}_2)_3\text{NH}_2]\) and phosphotungstic acid \((\text{H}_3\text{PW}_{12}\text{O}_{40})\) to a mesoporous silica. Catalyst 3 drove the tandem decacetalization–Henry reaction and decacetalization–Knoevenagel reaction of 4 with nitromethane and malononitrile to give trans-1-nitro-2-phenylethylene 5 and benzylidene malononitrile 6 in 92% and 91% yield, respectively.

Comment: The acid/base properties were controlled by the ratio and surface concentration of an amino group and phosphotungstate. Catalyst 3 was characterized by XANES \(\text{X-ray absorption near-edge structure spectrum}\), BET, BJH, $^{31}\text{P}$ NMR, $^{29}\text{Si}$ and $^{13}\text{C}$ CP-MAS NMR spectroscopy and GC-MS. Catalyst 3 was recovered by filtration and reused several times without significant loss of catalytic activity (4th use: 5 in 90% isolated yield, 6 in 91% isolated yield).