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Catalytic Meerwein-Ponndorf-Verley reductions over mesoporous silica supports: Rational design of hydrophobic mesoporous silica for enhanced stability of aluminum doped mesoporous catalysts

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ABSTRACT

A series of aluminum isopropoxide-grafted mesoporous organosilica having ethane ($-CH_2-CH_2-$) and ethene ($-CH{=}CH-$) groups in the frame wall positions (ethane–silica, ethene–silica) as well as mesoporous silicas (MCM-41, MCM-48, SBA-15) through siloxide linkages were fabricated. The samples were used as catalysts in the Meerwein-Ponndorf-Verley reduction of ketones and aldehydes of different nature and size using secondary alcohols as the hydrogen transfer agents. Aluminum isopropoxide supported mesoporous silica samples show higher catalytic conversion and among them, the one-dimensionally channel oriented Si-MCM-41 supported aluminum isopropoxide shows better results than the three-dimensional Si-MCM-48 and the large pore Si-SBA-15. Compared to aluminum isopropoxide-grafted mesoporous silica samples, aluminum alkoxide-grafted organosilica samples shows better catalytic activity even in the presence of 10% of water and the better stability is attributed to the presence of integrated hydrophobic organic groups in the frame wall positions.

1. Introduction

The Meerwein-Ponndorf-Verley (MPV) reduction of carbonyl compounds to primary and secondary alcohols involves equilibrium driven, reversible hydride transfer from a secondary alcohol, to a carbonyl substrate *via* a six-membered transition state, initiated by the activation of the carbonyl groups by coordination to the Lewis acidic aluminum centre [1–3]. The classical MPV reduction reaction is carried out in the presence of aluminum alkoxides like $Al(O^iPr)_3$ and ^iPrOH hydride source which offers many practical advantages like the mild reaction conditions, safe and simple operations and chemo selective nature—that unsaturated aldehydes and ketones are not reduced to saturated alcohols. However, the usage of stoichiometric amount of aluminum alkoxides, need for excess alcohols, low reaction rate due to the poor reactivity of traditional aluminum catalyst, as well as the formation of condensed products limits its wide applicability [4,5]. Hence, a high reaction temperature with the concurrent removal of the byproduct acetone from the system was applied so as to shift the equilibrium towards the formation of alcohols; but these in turn enhance side reactions like aldol condensation or the Tishchenko reactions [6].

Because of these reasons, a variety of aluminum catalysts are employed for the MPV reduction reactions. Simple alkyl aluminum reagents like $AlMe_3$ or $AlEt_3$ had shown very high activity in the MPV reductions and the high activity is attributed to the *in situ* formation of aluminum alkoxide species in the presence of excess isopropanol [7]. These results indeed show that elaborate ligands are not needed for obtaining high activity and selectivity in reduction reactions. Ooi et al. used a bidentate aluminum catalyst for the reduction process and had shown the reduction of a wide range of ketones and aldehydes in good yields [8]. Various other metal alkoxides, like the lanthanum alkoxides, are also used as catalysts for the reduction of carbonyl compounds [9,10]. However, many of these catalysts are homogenous and because of the difficulties associated with separating the products from the catalyst and from any reaction solvent urged for stable, recyclable solid catalysts. VanBekkum and colleagues found that zeolite beta catalyze the reduction of 4-*tert*-butyl cyclohexanone with a high stereo selectivity to the *cis*-isomer and had shown that Lewis acid sites are the active catalytic sites [11–15]. Subsequently, numerous metal oxides with acidic as well as basic properties are also found active in the reduction process [16–19]. Very recently, Corma et al. had shown that Sn-Beta and Zhu et al. had shown that Zr-beta and zirconium propoxide-grafted SBA-15 samples are efficient catalysts for the MPV reduction

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of different substrates [20–24]. The recent developments in heterogeneous MPV reduction reactions have been reviewed recently [25–27].

Periodic mesoporous organosilicas are remarkable organic–inorganic hybrid materials having organic moieties as molecularly bridging ligands in the frame wall positions; having a homogeneous distribution of organic fragments and silica moieties within the framework [28–30]. These materials show hydrophobic surfaces and consequently improve the hydrothermal stability applicable in diverse applications. Potential importance of organofunctionalized periodic mesostructures depends critically on the loading of accessible functional species in the network. Sulfonic acid functionalities for application in solid acid catalysis are reported whereas, amine functionalized hybrid mesoporous silicas finds their application in knoevenagel condensation reactions [31–35]. In addition, the titanium incorporated mesoporous hybrid silicas have demonstrated their potential in oxidative catalysis wherein the catalytic activity highly depends on the hydrophobicity of the materials [36–38]. Hence, in order to realize the full potential of the MPV reduction, the feasibility of supporting the aluminum isopropoxide over hydrophobic mesoporous organosilicas is attempted over the ethane ($-CH_2-CH_2-$) and ethene ($-CH{=}CH-$) bridged organosilicas and their stability was compared to a silylated mesoporous MCM-41 sample and conventional mesoporous silica supported $Al(O^iPr)_3$ catalyst (Scheme 1). Further, even though a variety of aluminum-containing catalyst was applied for MPV reduction, the truly active aluminum species is still not well understood and the stability of the supported aluminum isopropoxide is not high enough for practical applications. For instance, the aluminum isopropoxide catalyst exists as a tetra nuclear aggregate in the crystalline state in which the six-coordinated aluminum centre is surrounded by three bridging $Al(O^iPr)_3$ groups, but in solution a mixture of species forms and their easy interconversions complicates the prediction of active reactive aluminum sites [39]. Therefore, the heterogenization of aluminum isopropoxide over solid supports is alluring as they maintain the high activity with better reusability and thereby avoids the complications due to homogeneous catalysis. The work probes in detail about the influence of different supports in the grafting of aluminum isopropoxide species, effect of secondary alcohols used for the reduction, effect of poisoning agents in the catalytic activity and the nature of aluminum species formed over various support surfaces.

2. Experimental

2.1. Synthesis of aluminum doped PMS and PMO supports

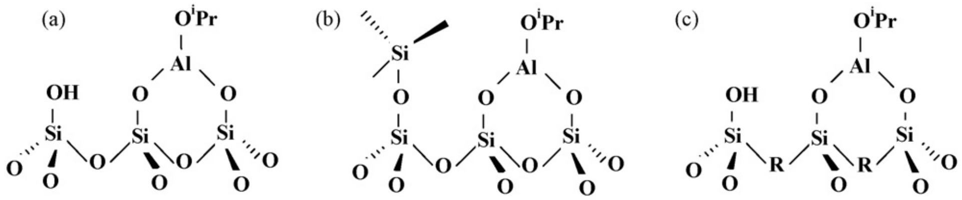
Periodic mesoporous silicas (PMS) and organosilicas (PMO) were prepared by known literature procedures and were described in detail in The Supporting Information. The grafting of aluminum isopropoxide over mesoporous MCM-41 support was carried out as follows. Typically for 2 wt.% loaded MCM-41 support material (2Al@MCM-41), the support (1 g, previously activated at 200 °C/6 h) was added to 30 ml of dry hexane. A solution of aluminum isopropoxide (0.15 g) in dry hexane (50 ml) was then added to the support material slowly with vigorous stirring. The suspension was then stirred at 80 °C for 12 h. The concentration of aluminum isopropoxide in dry hexane was varied so as to obtain 5% and 10% aluminum in the mesoporous samples. The product obtained was then filtered, washed with hexane to remove any unreacted precursors. The material was then dried in vacuum and kept in a vacuum desiccator before it gets used in the reaction. A similar procedure was carried out over other supports like MCM-48, SBA-15, amorphous silica gel and organosilica samples and for the synthesis of vanadium-, titanium- and zirconium-grafted MCM-41 supports. The aluminum-grafted MCM-41 materials were denoted as *x*Al@MCM-41, where *x* stand for the input Al wt.%.

2.2. Characterization

PXRD patterns of the mesoporous samples were recorded on a Rigaku D MAX III VC instrument using Ni-filtered Cu Kα radiation, between 1.5° and 10° (2θ), with a scanning rate of 1°/min. The amount of carbon content was evaluated by elemental analysis using EA1108 Elemental Analyzer (Carlo Erba Instruments) and the amount of aluminum loading was determined by an inductively coupled-plasma optical-emission-spectrometer (ICP-OES), after solubilization of the samples in HF–HCl solutions. TEM analyses of the mesoporous samples were performed on a JEOL-JEM-1200 EX instrument, at an accelerated voltage of 120 kV. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer after evacuation of the samples at 200 °C for 6 h. Pore size distribution (PSD) was obtained from the adsorption branch of the isotherm using Barrert–Joyner–Halenda (BJH) method. The nature of acid sites (Brönsted and Lewis) of metal-containing mesoporous catalyst was characterized by ex situ FT-IR spectroscopy with chemisorbed pyridine. A freshly activated catalyst powder sample was saturated with pyridine vapors placed in a desiccator containing pyridine. The pyridine-saturated sample was then activated at 150 °C for 2 h and the FT-IR spectra of the sample were recorded on a Shimadzu (Model-820PC) spectrometer under DRIFT mode. A similar procedure was used for the adsorption of cyclohexanone where instead of pyridine the probe molecule is changed to cyclohexanone. Solid-state ^{13}C CP MAS NMR, ^{29}Si MAS NMR and ^{27}Al MAS NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with a resonance frequency of 75.5, 59.6 and 104 MHz for ^{13}C, ^{29}Si and ^{27}Al using 4 mm zirconia rotors and a sample spinning frequency of 3 kHz. ^{13}C spectra were collected with 70° rf pulses, 5 s delay while ^{29}Si spectra were collected with 70° rf pulses, 30 s delay and in both cases with ~6000 scans. The chemical shifts were referenced to glycine, TMS and $[Al(H_2O)_6]^{3+}$ respectively, for ^{13}C and ^{29}Si and ^{27}Al.

2.3. Catalytic MPV reduction reactions

MPV reduction reactions were performed in a 10 ml round bottom flask immersed in a thermostated oil bath equipped with a



Scheme 1. Schematic representation of the grafting of $Al(O^iPr)_3$ catalyst over different mesoporous silica catalysts, (a) Si-MCM-41, (b) silylated Si-MCM-41 and (c) PMO.