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Short Communication

Unprecedented oxidative properties of mesoporous silica materials: Towards microwave-assisted oxidation of lignin model compounds

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ABSTRACT

The unusual oxidative ability of mesoporous silicas towards oxidation of an important lignin model molecule, 1,2-(4-hydroxy-3methoxy-phenoxy) ethanol, apocynol under microwave irradiation is presented in this work. Mesoporous MCM-41, HMS, SBA-15 and amorphous silica were employed as catalysts in the present study. Different reactivities were obtained for the various silica materials. It was assumed that the substrate conversion and product selectivity were highly influenced by the nature of mesoporous silica materials. Based on the nature of the catalysts and reaction product profile, a plausible mechanism has been proposed.

1. Introduction

Mesoporous silicate materials have gained an increased attention in the past decades owing to their interesting properties that include tunable pore sizes, stabilities and shape selectivity [1]. These materials have extensively been employed in a range of applications including adsorbency, catalysts, support and advanced materials [2]. Commonly, the basic silicate structures have been modified by inserting catalytically-functional groups such as metal ions or metal complexes in order to improve their adsorption and catalytic properties. The large abundance of internal surface hydroxyl groups facilitates anchoring/grafting catalytically active groups. Pure silica or silicates displaying catalytic behavior are rather unusual due to the low acidity of silanol groups and have been reported only in exceptional cases [3]. Morasas and Harrington have reported the oxidation behavior of quartz towards aerial oxidation of organic compounds [4] but the reaction mechanism is still unclear [5]. In a recent report, Itoh et al. have also studied the photocatalytic decarboxylation of organic compounds catalyzed in the presence of mesoporous silicas [6].

In this work, we present the unusual oxidation ability of mesoporous silica materials towards a lignin model compound (apocynol) under microwave irradiation. The proposed approach is highly promising as it employs conventional silicates as catalysts without any of the typical active species reported in redox heterogeneous catalysis [7,8]. We have utilized three representative ordered mesoporous silicas such as MCM-41, HMS and SBA-15 as catalysts. For comparative purposes, we have used commercial grade mesoporous silica as catalyst, which is amorphous in nature. The molecule studied [1,2-(4-hydroxy-3methoxy-phenoxy) ethanol] is an important lignin model phenolic monomer which has been largely investigated in order to understand the reactivity of lignin and lignin derived molecules. Recently, we have demonstrated that functionalized mesoporous silica materials can be used as efficient catalysts in the selective oxidation of the monomer [9,10] under microwave activation.

2. Experimental

Mesoporous silica catalysts; MCM-41, HMS and SBA-15 were prepared according to previously reported protocols [11–13]. Commercial grade mesoporous silica (Silica-5, Grace, Germany) was also used as catalyst. Apocynol was synthesized and characterized following the procedure outlined elsewhere [6]. Acetovanillone and vanillin (Aldrich) and 2-methoxybenzoquinone (TCI) were used as received.

Materials were characterized using X-Ray powder diffraction (XRD), TG-DTA and nitrogen physisorption measurements as described elsewhere [11–13]. ICP/MS experiments were conducted with typically 25 mg of sample digested in a mixture of aqueous HF, HNO_3 and HCl at 1:1:1 ratio. Upon dissolution, the sample was transferred to a 250 mL calibrated flask, diluted with miliQ water (to a maximum

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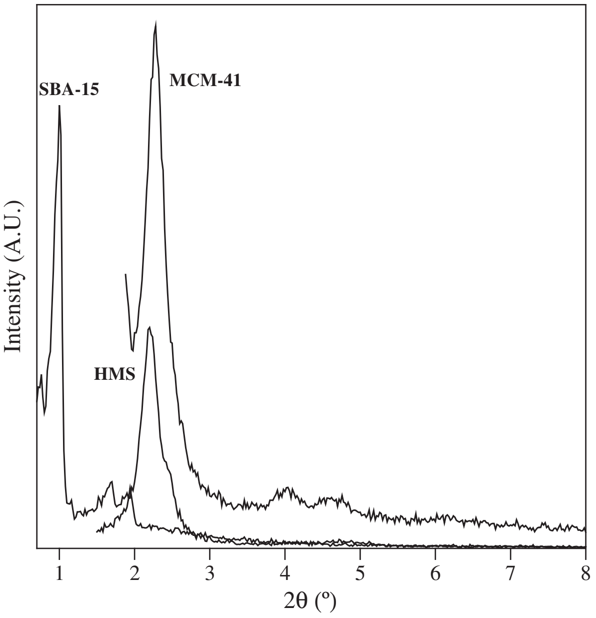
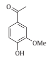
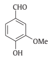
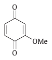
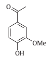
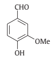
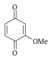


Fig. 1. XRD patterns of the investigated mesoporous materials.

Table 1
Oxidation of apocynol over mesoporous silica catalysts.

Entry	Catalyst	Conversion (%)	Product yield (%)			Product selectivity (%)		
			 **2**	 **3**	 **4**	 **2**	 **3**	 **4**
1	Blank	–	–	–	–	–	–	–
2	MCM–41	72	18	5	23	39	11	49
3	HMS	16	6	–	–	>99	–	–
4	SBA–15	36	18	–	–	>99	–	–
5	Silica–5	94	10	–	11	47	–	53

–Only traces of the product were observed.

content of 1% HF) and subsequently analyzed using an Elan DRC-e (PerkinElmer SCIEX) instrument (sensitivity > 0.05 ppm metal).

2.1. Catalytic activity studies

GC analyses were carried out on a Varian 3800 instrument, equipped with an autosampler and a DB-5 column (30 m × 0.32 mm × 0.25 μm film thickness) using nitrogen as the carrier gas. The initial column injector was set to 300 °C with an initial column temperature of 60 °C, raised to 150 °C with a ramp rate of 15 °C min^{-1} and then to 290 °C at 25 °C min^{-1} for 11.6 min. Identification of 2, 3 and 4 was carried out by comparison with authentic samples (GC and GC–MS).

Substrate conversion and product selectivity were determined using an external standard method, with decane as external standard. Response factors were obtained by preparation of known concentration samples of authentic materials and all data gave an excellent fit with an R^2 of 0.99 for all four materials.

In a typical catalytic reaction, apocynol (1.0 mmol, 168 mg), acetonitrile (5.0 mL), the catalyst (100 mg) and 35% aqueous H_2O_2 (0.34 mL, 3.0 mmol) were placed on a microwave tube and irradiated at 300 W on a CEM discover microwave reactor for 30 min.

3. Results and discussion

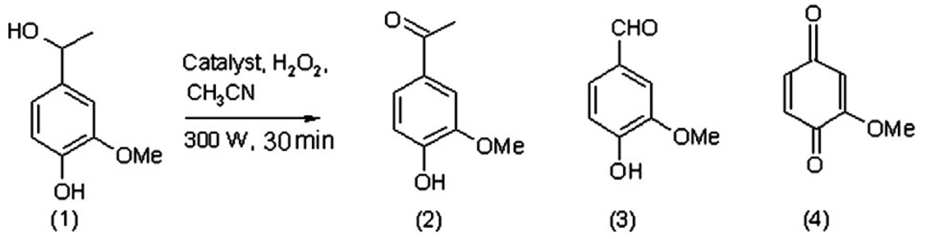
3.1. Characterization of materials

XRD pattern of calcined SBA-15, MCM-41 and HMS are shown in Fig. 1. Low angle strong reflection observed at 2θ = 0.98 and several weak reflections in the 2θ = 1.56–3.0 range, indicative of hexagonal mesoporous order (Fig. 1a). Similarly, Fig. 1b and c depict the structure of HMS and MCM-41 respectively. The XRD patterns of Silica-5 (not reproduced here) showed broad reflections between 2θ = 20–27°, with a clear indication of the amorphous nature of the material.

3.2. Catalytic experiments

Oxidation of apocynol (**1**) resulted in the formation of acetovanillone (**2**), vanillin (**3**) and 2-methoxybenzoquinone (**4**) (Scheme 1). Acetovanillone is the first oxidation product, vanillin is a product of side chain cleavage and 2-methoxybenzoquinone is generally formed through oxidation of the phenolic group together with oxidative degradation of the *p*-alkyl side chain [14]. Blank microwave runs of **1** without the catalyst gave no conversion after 30 min (Table 1). Reactions performed with chromatographic silica as catalyst resulted in the highest conversion among the studied catalysts with equal selectivity to **2** and **4**. Comparatively, MCM-41 provided very good conversion in the systems, with a superior selective towards **4**, while SBA-15 and HMS produced **2** with complete selectivity. These results indicate that the adsorption and catalytic performance of these materials are significantly influenced by their pore structure and internal surface. Schofled et al. stated in their work that impurities present in silicas were likely to be responsible from the observed oxidative properties [5]. Catalytic activities were significantly reduced upon acid pretreatment (to remove metal impurities). In contrast, ICP/MS determination of traces of metals in all materials showed that no quantifiable amounts of metals could be detected in the materials, meaning that traces of metals (if any) were in any case below <0.05 ppm. Pre-heating the materials prior to the reaction (which was previously reported to reduce the hydroxylation activity of the silica materials [5]) did not have any either significant effect on the observed catalytic activity in the materials. Based on these findings, and with surface hydroxyl groups as only common functionality to all materials, these groups could be assumed to be the active sites for the oxidation reaction.

The different distribution of Q_3 and Q_4 silanol groups in the materials has been included in Table 2 to facilitate a comparison of the materials in terms of hydroxyl-type of functionalities.



Scheme 1. Oxidation of apocynol under microwave irradiation.