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LA-CONTAINING SBA-15/H_2O_2 SYSTEMS FOR THE MICROWAVE ASSISTED OXIDATION OF A LIGNIN MODEL PHENOLIC MONOMER

Xiaoli Gu[1] , Ming He[1], Yijun Shi[1], Zhongzheng Li[1]

ABSTRACT

A convenient and efficient application of heterogeneous Lanthanum-containing SBA-15 systems for the microwave assisted oxidation of a lignin model phenolic monomer, 3-methoxy-4-hydroxybenzyl alcohol, is reported. Environmental friendly and low-cost H_2O_2 was used as the oxygen atom donor. The catalyst was prepared by immobilizing Lanthanum species on to the periodic mesoporous channels of siliceous SBA-15. Powder X-ray diffraction data and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) revealed that the host retains its hexagonal mesoporous structure after immobilization and most of the lanthanum species are better dispersed in the calcined materials. The surface area and pore size of La/SBA-15 was considerably decreased indicating the intrapore confinement of the Lanthanum species. The activity of the La/SBA-15 was investigated in the oxidation of 3-methoxy-4-hydroxybenzyl alcohol in the presence of hydrogen peroxide as oxidant. 68% conversion of 3-methoxy-4-hydroxybenzyl alcohol to vanillin or other undetectable by-products was obtained after 30 min of reaction under 200W microwave irradiation, compared to a poor 25% degradation after 24 h under conventional heating. The possibility of recycling the catalyst was studied.

Keywords: Lanthanum/SBA-15, lignin model compound, heterogeneous catalysis, microwave oxidation

INTRODUCTION

As a three dimensional amorphous plant poly-phenol, lignin is the second most abundant biopolymer on earth (Wool and Sun 2005). Currently, the vast majority of lignin is burned without any industrial application. Increasing research efforts have been made over the past few years to develop environment-friendly processes, for example, by the use of oxygen, hydrogen peroxide (H_2O_2), and ozone as primary oxidants. Due to the formation of radical intermediates, the conventional chemical oxidation of lignin leads to a poor selectivity and final product yield. Microwave assisted reactions can be highly efficient and polluteless, allowing a reduction in reaction time and energy consumption together with an increase in yields and selectivity in some cases (Conesa *et al.* 2007; Kappe 2008). Therefore, microwave assisted selective catalytic process based on a concerted oxygen atom transferred from H_2O_2 might solve these problems with water as the only by-product.

Since 1990s, the discovery of a new family of ordered mesoporous silica materials has sparked considerable interest because of their regular pore array with uniform pore diameter (2.0-8.0 nm), high surface area and pore volume (Kresge *et al.* 1992). In the family of mesoporous molecular sieves, SBA-15 exhibits larger pore sizes and thicker pore walls compared with other materials (Zhao *et al.* 1998a). Highly ordered SBA-15 or SBA-15 modified with some noble metals has become in recent years an important catalyst for a variety of synthetic transformations, such as selective oxidation of styrene, cyclohexane and total oxidation of toluene (Reddy *et al.* 2009; Bendahou *et al.* 2008; Zhang *et al.* 2007).

As an important promoter, the rare-earth elements have been used widely in the catalysts (Cui *et al.* 2006; Ma *et al.* 2006; Jia *et al.* 2008). Amongst the rare-earth elements, Lanthanum is the most common and important element to be used as catalysis material.

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In the present work, we report the synthesis of Lanthanum-containing SBA-15 mesoporous molecular sieves by a direct synthesis method in an acid medium. The properties of La/SBA-15 were characterized by powder X-ray diffraction (XRD) and N_2 adsorption-desorption analysis. The most commonly studied lignin model phenolic monomer, 3-methoxy-4-hydroxybenzyl alcohol, was chosen as target molecule and its oxidation was investigated with a heterogenised La/SBA-15 catalyst and microwave irradiation. The use of model compounds enables optimum (typically catalytic) conditions to be more easily determined on more complex lignin derived substrates. To the best of our knowledge, few studies dealing with the use of immobilized La-containing SBA-15 for the oxidation of lignin model compounds have been reported (Badamali *et al.* 2009).

MATERIALS AND METHODS

Materials

Standard agents for GC analysis were as follows: 3-methoxy-4-hydroxybenzyl alcohol (1), vanillin (2), 3-methoxy-4-hydroxybenzoic acid (3) and 2-methoxybenzoquinone (4) (Merk).

Preparation of La/SBA-15.

La/SBA-15 was prepared using a direct synthesis procedure according to the procedure reported by Zhao *et al*. (1998a) with minor modifications.

Two g triblock poly(ethylene oxide)$_{20}$-poly(propylene oxide)$_{70}$-poly(ethylene oxide)$_{20}$ (P123, average molecular mass about 5800, Aldrich) and 0.5 g lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$) were dissolved in a mixture of 35 mL 2 mol·L^{-1} HCl and 15 mL deionized water (pH≈1) under stirring. Then 4 g of tetraethyl orthosilicate (TEOS) were added to this solution (the molar ratio of La/Si = 1/20). The mixture was kept under continuous agitation at 40 ºC for 24 h. Then the gel was transferred to a Teflon-lined stainless steel autoclave and aged at 100 ºC for 24 h. The solid product was recovered by filtration and repeated washing with deionised water, followed by drying at 50 ºC overnight. The P123 template was removed by calcining at 550 ºC for 8 h in air. The SBA-15 material without lanthanum species was also prepared as reference according to Zhao *et al.* (1998a) for comparison.

The X-ray diffraction (XRD) analysis were performed on a D5000 Siemens powder diffractometer equipped with CuKα radiation (40KV and 30mA). The scattering intensities were measured over an angel range of $0° < 2\theta < 4°$ with a step size $\Delta(2\theta) = 0.02°$ and a step time of 8 s.

The N_2 adsorption/desorption isotherms were measured on a Micromeritics ASAP2010 at liquid N_2 temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by the BET (Brunauer – Emmett – Teller) method (Brunauer *et al.* 1938) and pore size distribution from the desorption isotherms by the Barrett-Joyner-Halenda (BJH) method (Barrett *et al.* 1951).

The ICP-AES was used to determine the content of La in the synthesized samples, which was performed on an Optima 4300DV. Before any measurements were taken, the solid sample was dissolved in 12 mL 0.1 mol·L^{-1} HCl solution mixed with 4 mL 1 mol·L^{-1} HF solution.

Catalytic activity studies

In a typical reaction, 3-methoxy-4-hydroxybenzyl alcohol (1.0 mmol, 154 mg), acetonitrile (5.0 mL), the catalyst (100 mg) and 35% aqueous H_2O_2 (0.34 mL, 3.0 mmol) were placed in a microwave tube and irradiated at 200W on a CEM discover microwave reactor for the time specified in Table 2. The same mixture in a round-bottomed flask was also reacted under conventional heating at 60 ºC for 24 h for comparative purposes. Reactants conversion and products yield were calculated as follows:

$$X_{\text{reactant}}(\%) = \frac{F_{\text{reactant,in}} - F_{\text{reactant,out}}}{F_{\text{reactant,in}}} \times 100\%$$

$$Y_{\text{product}}(\%) = \frac{F_{\text{product,out}}}{F_{\text{reactant,in}}} \times 100\%$$

$F_{i,in}$ and $F_{i,out}$ are the molar flow rate of the i species for reactant and product at the inlet and at the outlet of the reactor, respectively.

GC analyses were carried out on Agilent 6890 GC system, equipped with a DB-17MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness) using nitrogen as carrier gas. The initial column injector was set to 300 ºC with an initial column temperature of 60 ºC, raised to 150 ºC with a ramp rate of 15 ºC/min and then 25 ºC/min to 290 ºC keeping for 15min. Substrate conversion and product selectivity were determined using external standard method, with n-decane as external standard.

RESULTS AND DISCUSSION

Synthesis of materials

XRD patterns of calcined SBA-15 and La/SBA-15 are shown in Figure 1. It exhibits three well resolved diffraction peaks with d = 10.3, 6.2, and 5.3 nm, which can be indexed as the (100), (110), and (200) reflections associated with *p6mm* hexagonal symmetry (Zhao *et al.* 1998b); d(100) spacing of 10.3 nm corresponds to a large unit cell parameter a = 11.9 nm ($a_0 = 2 \times d_{100} / \sqrt{3}$). Figure 1b shows the XRD La-containing SBA-15 and the reflections are marginally shifted toward 2θ values which confirmed the immobilization of the La complex within the ordered SBA-15 structure (Kureshy *et al*. 2006).

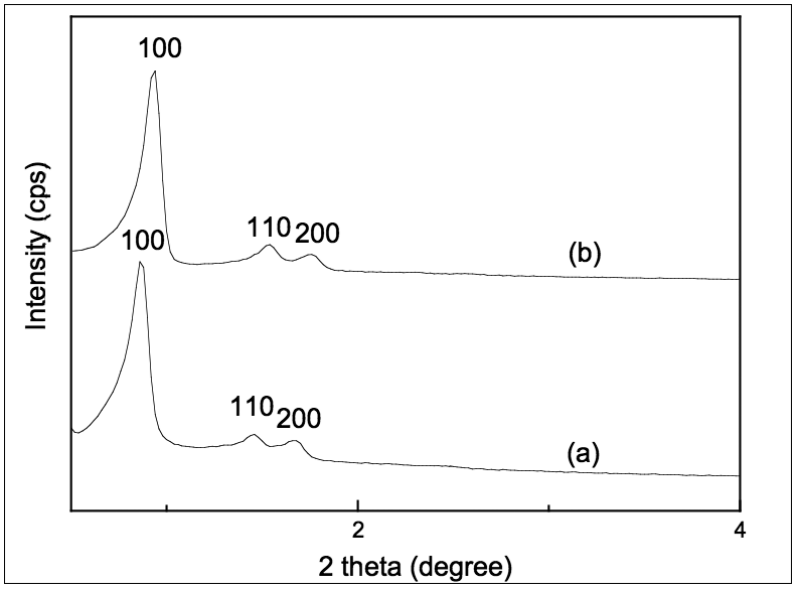

Figure 1. Powder XRD patterns of calcined SBA-15(a) and La/SBA-15(b)

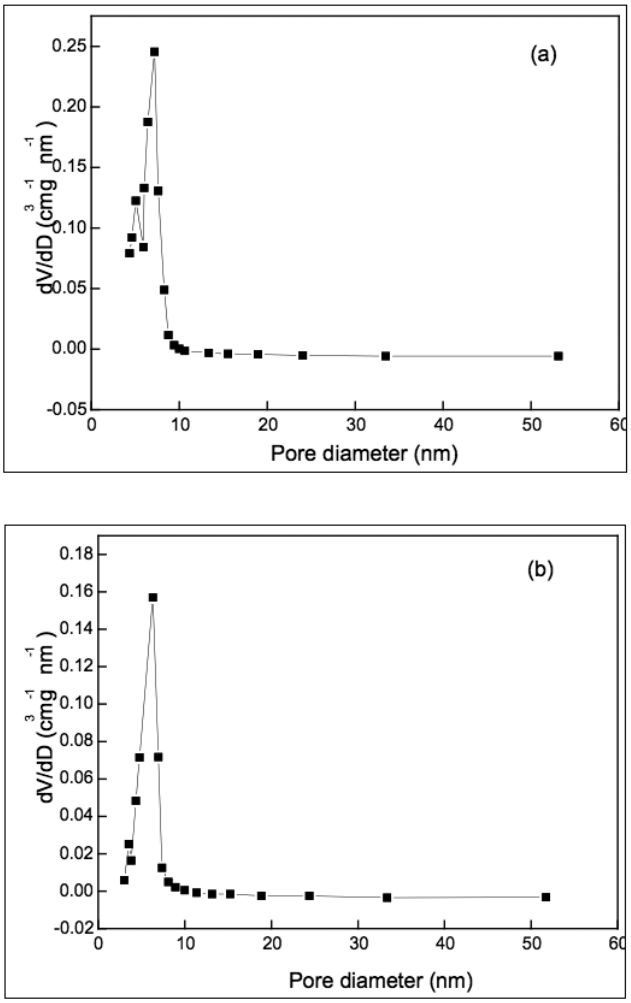

Figure 2. Nitrogen adsorption-desorption isotherms for SBA-15(a) and La/SBA-15(b)

For the N_2 adsorption-desorption isotherms for siliceous SBA-15 and La/SBA-15 (Figure 2-3), typical irreversible type IV adsorption isotherms with a H1 hysteresis loop as defined by IUPAC (Sing *et al*. 1985), were observed. This H1-type hysteresis loop suggests that the material has regular mesoporous channels with narrow Gaussian pore size distribution centred at 7.2 nm for siliceous SBA-15, at 6.3 nm for La/SBA-15 (Table 1). In fact, the main pore diameter decreased as the percentage of lanthanum species increased, which is in agreement with those published by other authors (Bendahou et al. 2008; Groen *et al*. 2003).

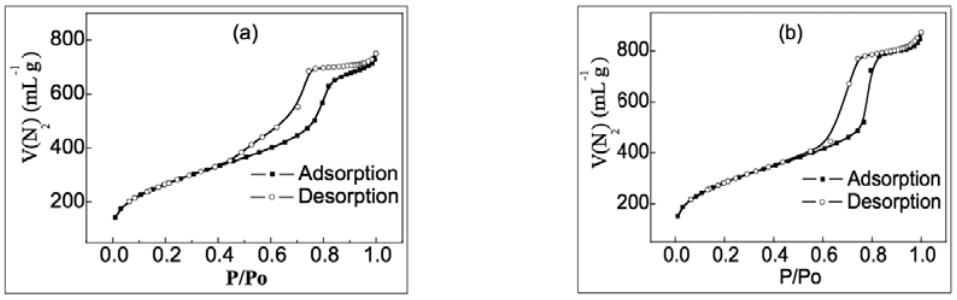

Figure 3. Pore size distribution patterns for SBA-15(a) and La/SBA-15(b)

Table 1. Physicochemical properties of SBA-15 and La/SBA-15 materials

Sample	Total S_{BET} [a] (m^2/g)	Total D_v [b] (m^3/g)	D_p [c] (nm)	a_0 [d] (nm)
SBA-15	780	1.1	7.2	10.6
La/SBA-15	566	0.9	6.3	11.9

[a] BET specific surface area

[b] Total pore volumes were obtained at P/P_0=0.99

[c] BJH pore diameter calculated from the desorption branch

[d] $a_0 = 2 \times d_{100} / \sqrt{3}$, a_0 calculated by d_{100}

The composition of solid products determined by ICP-AES is also listed in Table 1. The results also show that the content of La in the solid sample measured by ICP-AES (La/Si≈1/100) is obviously lower than of the initial gel mixture (La/Si=1/20), indicating a very small quantity of the solubility of lanthanum nitrate in the strong acidic medium. This indicates that the lanthanum species in the gel cannot be introduced completely into SBA-15 under some acidic conditions.

Catalytic experiments

Oxidation of 3-methoxy-4-hydroxybenzyl alcohol (1) resulted in formation of vanillin (2), 3-methoxy-4- hydroxybenzoic acid (3) and 2-methoxybenzoquinone (4) (Figure 4). Vanillin is the first oxidation product, while 3-methoxy-4-hydroxybenzoic acid and 2-methoxybenzoquinone are formed through oxidation of the phenolic group together with further oxidation.

Table 2 includes results of the oxidation of 3-methoxy-4-hydroxybenzyl alcohol using La/SBA-15 at different times with changeable temperature (<423K) under microwave irradiation. Only traces of detectable low molecular weight products such as vanillin were observed at short times of reaction (<5min). About 68% of substrate conversion was observed with an optimum yield to vanillin within 30 min of reaction. Complete oxidation of 3-methoxy-4-hydroxybenzyl alcohol was observed after 40 min with high molecular weight compounds perhaps including phenolic dimers and quinones, which was also mentioned in previous reported results (Crestini *et al.* 2005).

Blank microwave runs of 1 (without catalyst and without H_2O_2; Table 2 entry 10) gave no conversion after 15 min and only 8% of substrate conversion was observed in the presence of H_2O_2 without catalyst (Table 2 entry 11). This clearly indicates that La/SBA-15 material catalyses the reaction. Interestingly, the support SBA-15 alone gave 34% of substrate conversion after 30 min, whereas 68% conversion was obtained using immobilized La/SBA-15 catalyst, compared to a poor 25% conversion after 24 h under conventional heating without microwave irradiation (Table 2, entry 12).

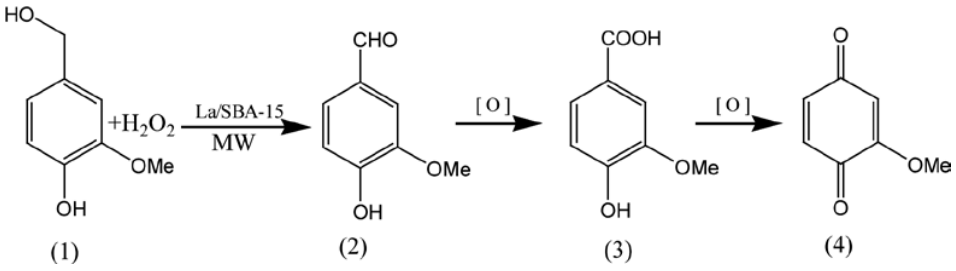

Figure 4. Product distribution in the oxidation of 3-methoxy-4-hydroxybenzyl alcohol (1)

Table 2. Oxidation of 3-methoxy-4-hydroxybenzyl alcohol (1) using La/SBA-15[a]

Entry	Time of reaction (min)	Substrate (1) Conversion (%)	Product distribution (%)			Product yield (%)		
			2	3	4	2	3	4
1	5	24.6	-[b]	-	-	-	-	-
2	10	35.9	-	-	-	-	-	-
3	15	41.1	100	-	-	15.6	-	-
4	20	57.2	100	-	-	13.7	-	-
5	25	62.7	100	-	-	11.8	-	-
6	30[1st]	67.8	100	-	-	10.6	-	-
7	35	84.1	65	-	35	13.1	-	5.2
8	40	95.1	51	-	49	6.0	-	4.6
9	30[c]	34.3	-	-	-	-	-	-
10	15[d]	<0.5	-	-	-	-	-	-
11	15[e]	7.9	-	-	-	-	-	-
12	1440[f]	25.1	-	-	-	-	-	-
13	30[2nd]	67.2	100	-	-	10.5	-	-
14	30[3rd]	65.9	100	-	-	10.0	-	-
15	30[4th]	63.1	100	-	-	9.6	-	-
16	30[5th]	63.5	100	-	-	9.6	-	-
17	30[6th]	60.1	100	-	-	9.3	-	-
18	30[7th]	50.7	100	-	-	7.5	-	-
19	30[8th]	43.6	100	-	-	5.6	-	-
20	30[9th]	35.8	100	-	-	-	-	-
21	30[10th]	30.7	100	-	-	-	-	-

[a] Microwave reaction conditions: 0.5 mmol 3-methoxy-4-hydroxybenzyl alcohol, 1.5 mmol H_2O_2, 3 mL acetonitrile, 0.1 g catalyst, microwave irradiation 200W

[b] Not detectable

[c] SBA-15 catalyst

[d] without catalyst and without H_2O_2

[e] without catalyst but with H_2O_2

[f] 60 ºC for 24 h, without microwave irradiation

entry 13-21 La/SBA-15 catalyst recycling performance for 2-10 times with the same reaction conditions as entry 6

The reusability of the catalyst was studied after isolation and subsequent activation of the catalyst after reaction completion (Table 2, Figure 5). The used catalyst in the first cycle of the reaction was separated by filtration, washed three times with ethanol, dried in an oven at 100 ºC for 24 h, and activated at 300 ºC for 4 h in air. The first recycling run provided similar activities of the catalyst with complete 3-methoxy-4-hydroxybenzyl alcohol oxidation after 30 min. Subsequent reuses gave very similar results with the active La/SBA-15 preserving most of its initial activity after 6 runs. It can be concluded that the catalyst can be reused at least 6 times and there is no appreciate loss in catalytic activity.

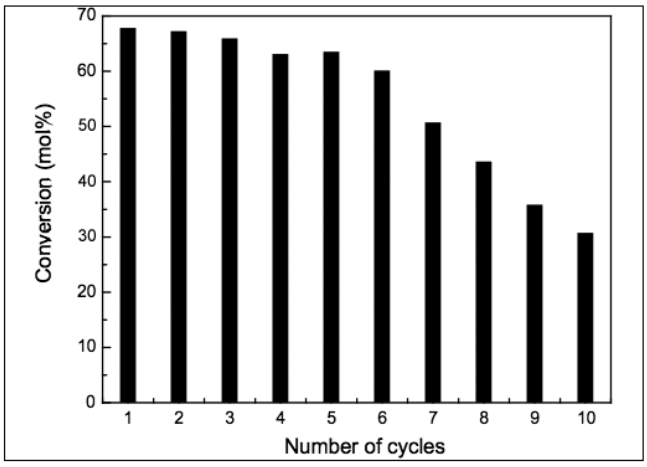

Figure 5. Recycling of the La/SBA-15 catalyst

CONCLUSION

For the first time we have demonstrated that mesoporous La/SBA-15 acts as an efficient catalyst for oxidation of an important lignin model compound. The active La species seemed to be stabilized within the mesoporous host, rendering unusual oxidative ability and excellent selectivity. The result is attributed to the presence of isolated hydroxyl groups and the meso-micro pore architecture, which provides an ideal environment for the reaction. Microwave assisted reactions were found to be efficient and selective as compared to the thermal reactions. The catalyst can be reused without significant loss in activity.

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