

PRODUCTION OF AROMATIC ALDEHYDE BY MICROWAVE CATALYTIC OXIDATION OF A LIGNIN MODEL COMPOUND WITH La-CONTAINING SBA-15/H₂O₂ SYSTEMS

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A convenient and efficient application of heterogeneous La-containing SBA-15 systems for the microwave assisted oxidation of a lignin model phenolic monomer, 4-hydroxy-1-phenylpropane, is reported. Low-cost and environmentally friendly H₂O₂ was used as the oxygen atom donor. The catalyst was prepared by immobilizing lanthanum species on the periodic mesoporous channels of siliceous SBA-15. Powder X-ray diffraction data and 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 4-hydroxy-1-phenylpropane in the presence of hydrogen peroxide as oxidant. 70.5% conversion of 4-hydroxy-1-phenylpropane was obtained after 30 min of reaction under 200W microwave irradiation, compared to a poor 28.1% degradation after 24h under conventional heating. The possibility of recycling the catalyst was studied.

Keywords: Lanthanum/SBA-15; Lignin model compound; Heterogeneous catalysis; Microwave oxidation

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INTRODUCTION

Lignin is an extremely complex three-dimensional macromolecule with irregular structure (Wool and Sun 2005). Currently, the vast majority of lignin is burned without any industrial utilization. However, a small amount of lignin is decomposed with traditional elemental chlorine or chlorine dioxide employed for the degradation of lignin, resulting in the formation of harmful poly-chlorinated compounds along with poly-phenolic residues. Consequently, increasing research efforts have been made over the past few years to develop environmentally friendly processes, for example, by the use of oxygen, hydrogen peroxide (H₂O₂), and ozone as primary oxidants. Due to the formation of radical intermediates, such as hydroxyl radicals during the degradation of lignin, the conventional chemical oxidation of lignin leads to a poor selectivity and final product yield.

Microwave technology has been the subject of extensive studies over the past few years, and many reports have appeared with application of microwave-assisted synthesis (Conesa et al. 2007). Microwave assisted reactions can be highly efficient and pollution-

free, allowing a reduction in reaction time and energy consumption, together with an increase in yields and selectivity in some cases (Kappe 2008). Therefore, a microwave assisted selective catalytic process based on a concerted oxygen atom transferred from H₂O₂ might solve these problems, with water as the only by-product.

Recently, 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 (2.0-8.0nm), high surface area, and high pore volume, which characterize the key active catalytic reaction site (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). Due to its mesoporous structure, higher wall thickness and good hydrothermal stability, SBA-15 materials are regarded as the most promising catalytic materials since their synthesis. 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, etc. (Reddy et al. 2009; Bendahou et al. 2008; Zang et al. 2007). However, the pure-silica mesoporous materials are limited in some catalytic reactions because of their lack of active sites. Thus, according to the requirement of various catalytic reactions, various components are introduced into the ordered mesoporous silica materials by various methods.

As an important promoter, the rare-earth elements have been applied widely in catalysts (Cui et al. 2006; Ma et al. 2006; Jia et al. 2008). Amongst the rare-earth elements, La is the most common and important element to be used as a catalysis material. 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 N₂ adsorption-desorption analysis. The most commonly studied lignin model phenolic monomer, 4-hydroxy-1-phenylpropane, was chosen as the target molecular, 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 for subsequent chemistry on more complex lignin-derived substrates. To the best of our knowledge, studies dealing with the use of immobilized La-containing SBA-15 for the oxidation of lignin model compounds have not previously been reported.

EXPERIMENTAL

Materials

The following material was used as the model compound:

4-hydroxy-1-phenylpropane (1) self-produced, >98%purity

The following compounds were used as standard agents for GC analysis:

p-hydroxybenzaldehyde (2),

p-hydroxybenzoic acid (3),

p-hydroxybenzoquinone (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. (1998) with minor modifications.

2g triblock poly(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀ (P123, average molecular mass about 5800, Aldrich) and a certain amount of lanthanum nitrate (La(NO₃)₃·6H₂O) were dissolved in a mixture of 35ml 2mol·L⁻¹ HCl and 15ml deionized water (pH≈1) under stirring, and the 4g of tetraethyl orthosilicate (TEOS) was added to this solution (the molar ratio of La/Si =5%). The mixture was kept under continuous agitation at 40°C for 24h. Then the gel was transferred to a Teflon-lined stainless steel autoclave and aged at 100 °C for 24h. The solid product was recovered by filtration and repeated washing with deionised water, followed by drying at 50 °C overnight. The P123 template was removed by calcining at 550 °C for 8h in air. The SBA-15 material without lanthanum species was also prepared as Zhao et al. (1998a) reported for comparison.

The X-ray diffraction (XRD) analyses were performed on a D5000 Siemens powder diffractometer equipped with a copper anode. The scattering intensities were measured over an angle range of 0°<2θ<4° with a step size Δ(2θ)=0.02° and a step time of 8s.

The N₂ adsorption/desorption isotherms were measured on a Micromeritics ASAP2010 at liquid N₂ temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by the BET method and pore size distribution from the desorption isotherms by the Barrett-Joyner-Halenda (BJH) method.

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 dilute HCl solution with a small amount of HF.

Catalytic Activity Studies

In a typical reaction, 4-hydroxy-1-phenylpropane (1.0mmol, 152mg), acetonitrile (5.0ml), the catalyst (100mg) and 35% aqueous H₂O₂ (0.34ml, 3.0mmol) were placed on a microwave tube and irradiated at 200W on a CEM discover microwave reactor for the time specified in Table 1. The same mixture in a round-bottomed flask was also reacted under conventional heating at 60 °C for 24h for comparative purposes. Reactants conversion and products yield were calculated as follows,

$$X_{\text{reactant } i} (\%) = \frac{F_{\text{reactant } i, \text{in}} - F_{\text{reactant } i, \text{out}}}{F_{\text{reactant } i, \text{in}}} \times 100 \quad (1)$$

$$Y_{\text{product}} (\%) = \frac{F_{\text{product, out}}}{F_{\text{reactant } i, \text{in}}} \times 100 \quad (2)$$

where $F_{i, \text{in}}$ and $F_{i, \text{out}}$ are the molar flow rate of the i^{th} species at the inlet and at the outlet of the reactor, respectively.

GC analyses were carried out with an Agilent 6890 GC system, equipped with a DB-17MS capillary column (30m×0.25mm×0.25μm 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 and then to 290 °C at 25 °C /min for 15min. Substrate conversion and product selectivity were determined using the external standard method, with decane as the external standard. The gas chromatogram diagram for standard samples was obtained as follows:

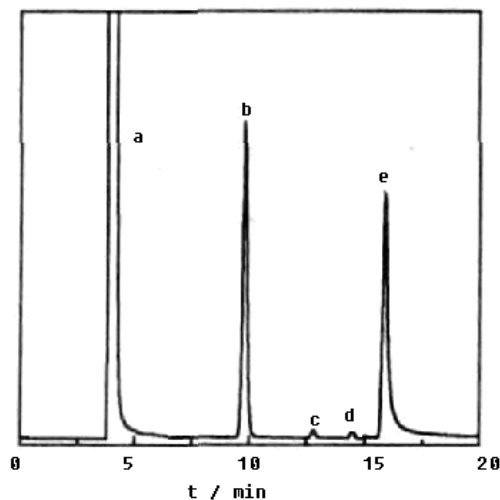


Figure 1. Gas chromatographic results, where the peaks were identified as follows: a: methanol(solvent), b: p-hydroxybenzaldehyde (2); c: p-hydroxybenzoic acid (3); d: p-hydroxybenzoquinone (4); and e: 4-hydroxy-1-phenylpropane (1)

RESULTS AND DISCUSSION

Synthesis of Materials

XRD patterns of calcined SBA-15 and La/SBA-15 are shown in Fig. 2. The diffractogram 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 were marginally shifted toward 2θ values, which confirmed the immobilization of the La complex within the ordered SBA-15 structure (Kureshy et al. 2006).

For the N_2 adsorption-desorption isotherms for siliceous SBA-15 and La/SBA-15 (Fig. 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 a narrow Gaussian pore size distribution centred at 7.2 nm for siliceous SBA-15, and at 6.3 nm for La/SBA-15 (Fig. 4). In fact, the main pore diameter decreased as the percentage of lanthanum species increased, which is in agreement with results published by other authors (Bendahou et al. 2008; Groen et al. 2003).

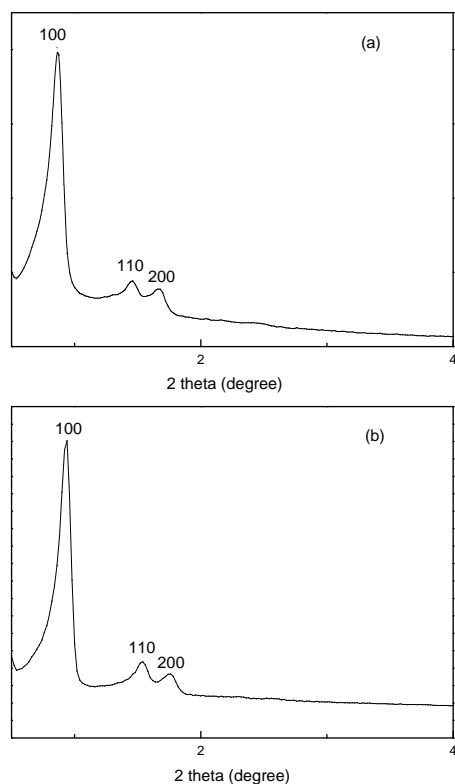


Fig. 2. Powder XRD patterns of calcined SBA-15(a) and La/SBA-15(b)

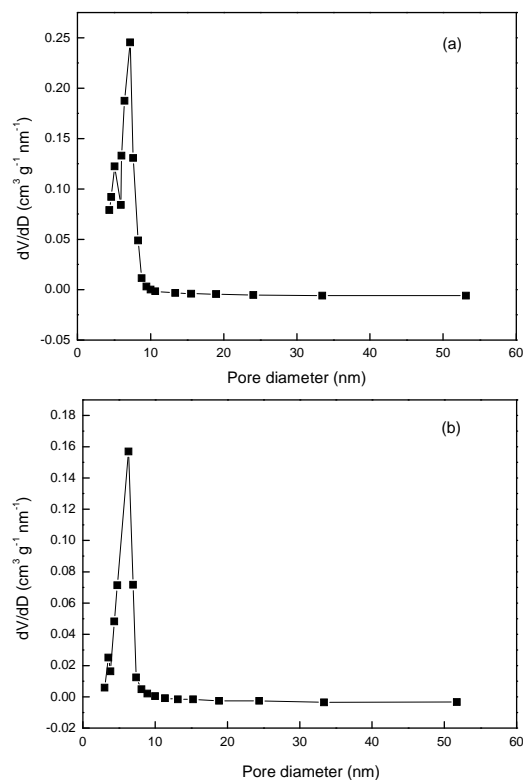


Fig. 3. Nitrogen adsorption-desorption isotherms for SBA-15(a) and La/SBA-15(b)

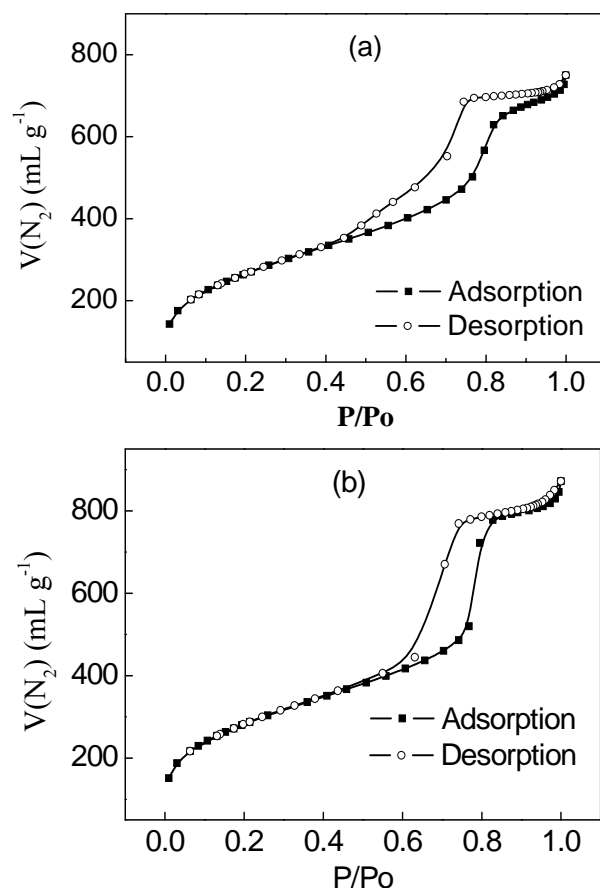


Fig. 4. Pore size distribution patterns for SBA-15(a) and La/SBA-15(b)

Table 1. Physicochemical Properties of SBA-15 and La/SBA-15 Materials

Sample	(La/Si) ^a gel(%)	(La/Si) ^b cal(%)	Total S _{BET} ^c (m ² /g)	Total D _v ^d (cm ³ /g)	D _p ^e (nm)	a ₀ ^f (nm)
SBA-15	-	-	780	1.1	7.2	10.6
La/SBA-15	5	1.18	566	0.9	6.3	11.9

^a La/Si (molar ratio) in gel mixture

^b La/Si (molar ratio) after calcinations, obtained by the ICP analysis.

^c BET specific surface area.

^d Total pore volumes were obtained at P/P₀=0.99

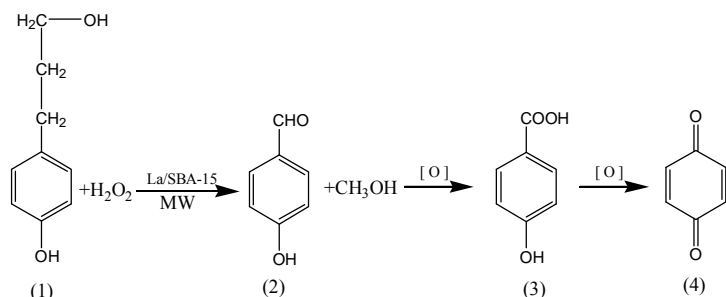
^e BJH pore diameter calculated from the desorption branch.

^f a₀ calculated by d₁₀₀, $a_0 = 2 \times d_{100} / \sqrt{3}$

The compositions of solid products determined by ICP-AES are listed in Table 1. The results also show that the content of La in the solid sample measured by ICP-AES was obviously lower than of the gel mixture, 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 4-hydroxy-1-phenylpropane (1) resulted in formation of p-hydroxybenzaldehyde (2), p-hydroxybenzoic acid (3), and p-hydroxybenzoquinone (4) (Scheme 1). p-hydroxybenzaldehyde is the first oxidation product, while p-hydroxybenzoic acid and p-hydroxybenzoquinone is formed through oxidation of the phenolic group together with further oxidation.



Scheme 1. Product distribution in the oxidation of 4-hydroxy-1-phenylpropane (1) under microwave irradiation

The aromatic aldehyde, the oxidative products from lignin in the catalytic process, can be further oxidized to aromatic acids, and even to high molecular weight compounds including phenolic dimers and quinines (Crestini et al. 2005). Figure 5 includes results of the oxidation of 4-hydroxy-1-phenylpropane using some catalysts including La/SBA-15 at different times of microwave irradiation. The rate of substrate conversion and yield of each of the oxidative products was significantly higher with the catalyst La/SBA-15 than that without the catalyst. In the absence of a catalyst, the substrate conversion was 14.3% at 30min, in comparison with 70.5% with La/SBA-15 as catalyst (Fig. 5a). The maximum yield of p-hydroxybenzaldehyde was 26.8% in 15 minutes with the La/SBA-15 catalyst, 10.7% higher than that of the noncatalytic process, whose maximum yield was 16.1% (Fig. 5b).

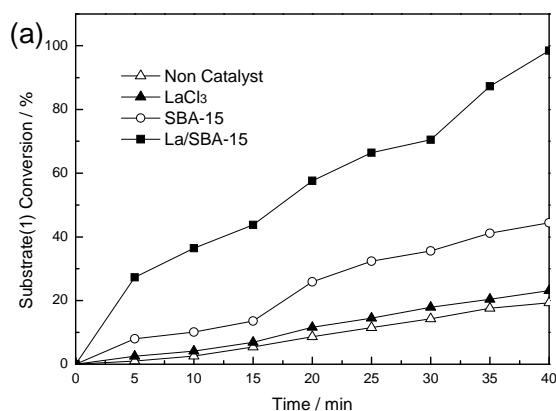


Fig. 5a. Substrate 4-hydroxy-1-phenylpropane conversion (a). The microwave reaction conditions: 0.5mmol 4-hydroxy-1-phenylpropane, 1.5mmol H₂O₂, 3ml acetonitrile, 0.1g catalyst, microwave irradiation 200W, in comparison to non-catalyzed process(△), 3% (W/W, on substrate) LaCl₃(▲), SBA-15(○), La/SBA-15(■) as catalyst in catalytic process at different reaction time.

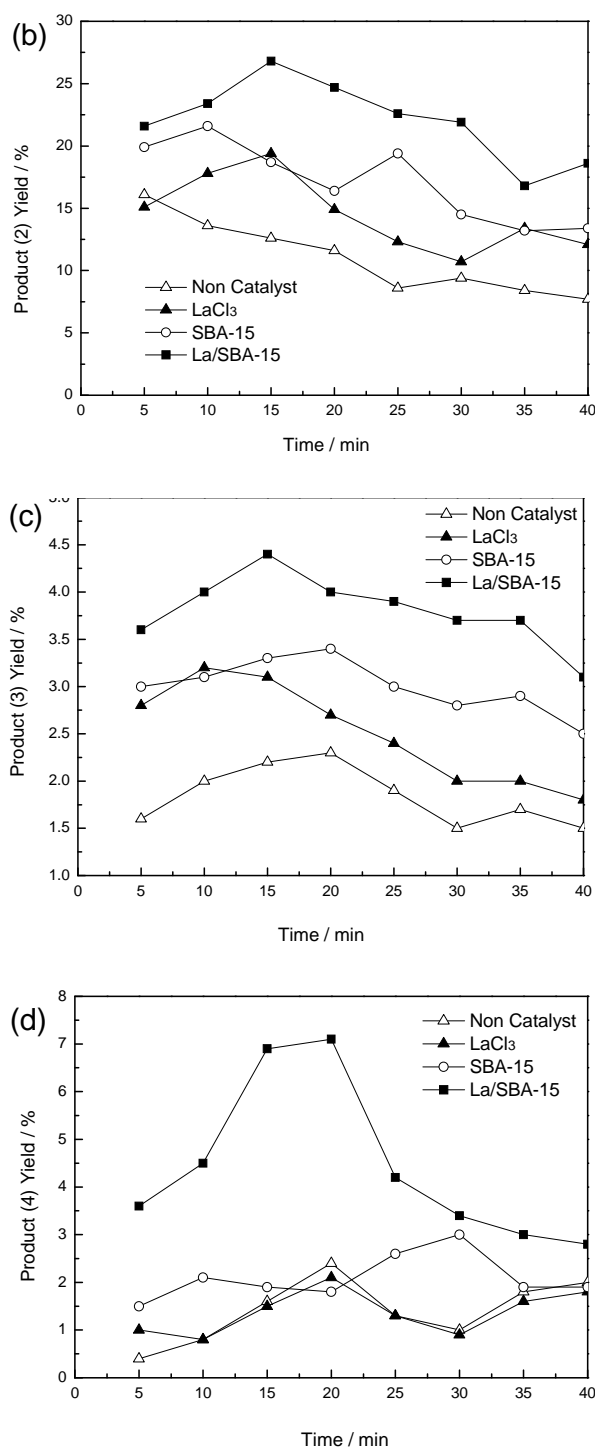


Fig. 5b-d. Yield of p-hydroxybenzaldehyde(b), p-hydroxybenzoic acid(c) and p-hydroxybenzoquinone(d) with reaction time. The microwave reaction conditions: 0.5mmol 4-hydroxy-1-phenylpropane, 1.5mmol H₂O₂, 3ml acetonitrile, 0.1g catalyst, microwave irradiation 200W, in comparison to non-catalyzed process(△), 3% (W/W, on substrate) LaCl₃(▲), SBA-15 (○), La/SBA-15(■) as catalyst in catalytic process at different reaction time.

Blank microwave runs of 1 (without catalyst and H₂O₂) gave no conversion after 15 min and only 5.4% of substrate conversion was observed in the presence of H₂O₂ without catalyst. The same concentration of LaCl₃ ion solution as that of La/SBA-15 exhibited modest catalytic activity, while the support SBA-15 alone gave 35.6% of substrate conversion after 30min. On the other hand 70.5% conversion was obtained using immobilized La/SBA-15 catalyst, compared to a poor 28.1% conversion after 24h under conventional heating reaction condition without microwave irradiation. This clearly indicates that La/SBA-15 material catalyses the reaction (Fig 5a-d).

The reusability of the catalyst was studied after isolation and subsequent activation of the catalyst after reaction completion (Fig. 6). 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 °C for 24h, and activated at 300 °C for 4h in air. The first recycling run provided similar substrate conversion with 4-hydroxy-1-phenylpropane oxidation after 30min. 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 and there is no appreciate loss in catalytic activity. However, subsequent reuses indicated the fall in the activity of La/SBA-15 after 6th run. Due to the loss of active sites of incorporated La ion over the catalyst, the lower catalytic activity was observed.

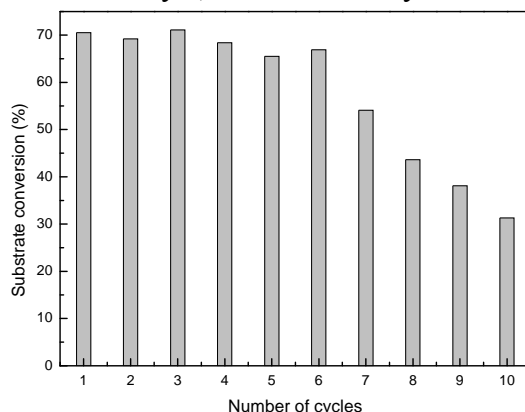


Fig. 6. Recycling of the La/SBA-15 catalyst

CONCLUSIONS

1. 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.
2. 70.5% conversion of 4-hydroxy-1-phenylpropane was obtained after 30 min of reaction under 200W microwave irradiation, compared to a poor 28.1% degradation after 24h under conventional heating. 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.
3. The catalyst can be reused more than 6 times without significant loss in catalytic activity.

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