Direct synthesis of lanthanide-containing SBA-15 under weak acidic conditions and its catalytic study

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Abstract

Lanthanide (Ln including La, Ce and Nd) containing SBA-15 molecular sieves with molar ratio $\text{Ln/Si} = 0.01\text{--}0.2$ were prepared via direct synthesis under weak acidic conditions (pH 1.5–3.0). Characterizations of these samples were done by powder X-ray diffraction, N_2 adsorption, inductively coupled plasma atomic emission spectrometry (ICP-AES), FT-IR spectroscopy, and diffuse reflectance ultra-violet spectroscopy. All the samples show a highly ordered two-dimensional hexagonal mesostructure. N_2 adsorption testifies that all the Ln-containing SBA-15 materials have the type IV isotherms with type H_1 hysteresis loop as well as high specific surface area (798–925 m^2/g) and narrow pore size distribution. The diffuse reflectance UV–vis, ICP-AES, and the wide-angle XRD spectra show that most of the lanthanide ions are better dispersed in the calcined materials. The Ln-SBA-15 supported Pd catalysts show high catalytic activity in the oxidation of benzene. The results reveal that Ln-SBA-15 materials can be used as potential supports for the catalytic oxidation of VOCs.

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1. Introduction

Since the discovery of MCM-41 materials by Mobil scientists [1], more and more efforts have been focused on the synthesis of mesoporous molecular sieves, such as SBA, HMS [2], FSM-16 [3], KIT-1 [4] and so on. Among all these mesoporous materials, SBA-15 is regarded as one of the most promising materials because of its higher surface area, larger pore size and higher hydrothermal and thermal stability. It is well known that pure silica SBA-15 is inert in catalytic reactions due to the absence of heteroatom activity sites. Therefore, many scientists have attempted to incorporate various atoms, such as Ti, V, Al, Cr, Fe, into

the framework or disperse them onto the surface of siliceous materials as metal or metal oxides, which can introduce catalytic sites into mesoporous materials [5–13].

Rare-earth elements have been widely used in the field of catalysis. They participate in the stabilization of supports against thermal sintering and enhance the performance of catalysts in storing and releasing oxygen as well as reducing the reaction activation energy. In recent years, lanthanide-containing porous materials have been reported and have shown good performance in catalysis. Othman and his coworkers have reported the higher decolorization activity of Mn-La/ZSM-5 than Mn/ZSM-5 [14]. Ce-containing MCM-41 shows good catalytic activity for the vapor-phase dehydration of cyclohexanol to cyclohexene and hydroxylation of 1-naphthol with aqueous H_2O_2 and *tert*-butyl hydroperoxide [15]. As we mentioned above, the ordered mesoporous structure and large pore size of SBA-15 are likely more favorable to the diffusion of reactants and

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products. Thus, lanthanide-containing SBA-15 should be regarded as good catalyst candidates for some catalytic reactions.

Preparation of catalysts with well-dispersed isolated metal species is crucial in achieving high activity and selectivity for catalytic reactions. The rare-earth oxides are usually coated on the wall of SBA-15 by the incipient wetness impregnation and grafting methods, which can result in the appearance of bulk metal species, blocking the channels of SBA-15 and affecting its catalytic activity [8–11,16]. Thus it is important to introduce an effective method to synthesize dispersed metal or metal oxides-containing SBA-15, such as the co-condensation or direct synthesis methods. Generally, SBA-15 is synthesized under strong acidic conditions, under which it is difficult to introduce the metal ions into the SBA-15 directly due to the difficulties in the formation of the metal–O–Si bonds. Recently, Li and coworkers reported the preparation of highly ordered Fe-SBA-15 under weak acidic conditions [7]. In their work, Fe substituted SBA-15 mesoporous materials with isolated iron species were obtained via simple direct-hydrothermal methods under pH 1.0–5.6. It has been indicated that iron ions are generally in an isolated state and it is more suitable to prepare highly isolated metal substituted SBA-15 mesoporous materials under acidic conditions, especially if these conditions are weak [17,6]. Thus, it is absolutely necessary to make an attempt to prepare dispersed lanthanide-containing SBA-15 using a similar method as reported in Li's paper.

In this work, lanthanide (Ln including La, Ce and Nd) containing SBA-15 mesoporous materials were directly synthesized under weak acidic conditions (pH 1.5–3.0). The synthesized materials are characterized by powder X-ray diffraction (XRD), N_2 sorption, UV–vis spectra analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis, and Fourier-transform infrared spectroscopy (FT-IR). The different Pd supported (support = Ln-SBA-15, Ce-Im-SBA-15, SBA-15 and γ - Al_2O_3) catalysts are further prepared by an incipient wetness method and tested the rate of the catalytic oxidation of benzene.

2. Experimental section

2.1. Materials preparation

Ln-SBA-15 materials were synthesized using tetraethyl orthosilicate (TEOS) and lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$), cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$), or neodymium nitrate ($Nd(NO_3)_3 \cdot 6H_2O$) as the silicon and lanthanide precursors respectively. Non-ionic triblock copolymer surfactant $EO_{20}PO_{70}EO_{20}$ (P123, Aldrich) was used as the structure-directing agent. Concentrated HCl solution was used as the acid source.

The typical preparation procedures of Ln-SBA-15 materials are described as follows: 1 g of P123 was dissolved into 35 ml HCl solution under different pH i.e. 1.5, 2.0, 2.5 or 3.0. Once P123 was completely dissolved, a certain amount of lanthanide nitrates (Ln/Si = 0.01–0.2) were added to the

above P123-HCl solution. Then, 2.3 ml of TEOS was added, followed by the addition of NH_4F (F/Si = 0.03), which was used to accelerate the hydrolysis rate of TEOS to match that of Lanthanide nitrates. The mixture was stirred vigorously for 2 h at room temperature and kept under static conditions for 24 h at 35 °C. The mixture was then transferred into an autoclave and aged for 48 h at 100 °C. The resulting solid was filtered, washed and dried at 100 °C for 24 h. The final mesoporous Ln-SBA-15 products were obtained after calcination at 550 °C for 6 h. Pure SBA-15 was prepared with the same method as Ln-SBA-15, except that no lanthanide nitrate was added to the P123-HCl solution.

Pd was loaded on Ln-SBA-15 via the impregnation method with palladium chloride as the precursor. 500 mg of Ln-SBA-15 (Ln/Si = 0.1) synthesized at pH 2.5 was added to the palladium chloride solution ($PdCl_2$: 1.25 mg/ml) and stirred at 70 °C. The obtained solid was calcined at 500 °C for 3 h and then reduced under hydrogen at 480 °C for 2 h. These catalysts were noted as Pd/La-SBA-15, Pd/Ce-SBA-15 and Pd/Nd-SBA-15. For comparison, Pd/SBA-15, Pd/Ce-Im-SBA-15 and Pd/ γ - Al_2O_3 were synthesized using the same method described above. For all the tested catalysts, the percentage of Pd was 0.9% and expressed as the weight ratio of $W_{Pd}/W_{Support}$.

2.2. Materials characterizations

XRD patterns were recorded on a SIEMENS D5005D powder diffraction system using Cu $K\alpha$ radiation over the range $0.7^\circ \leq 2\theta \leq 6.0^\circ$. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature, using a NOVA1200 gas sorption analyzer. Prior to the measurements, all samples were degassed under vacuum at 300 °C for 5 h. The specific surface area, A_{BET} , was determined from the linear part of the BET equation ($P/P_0 = 0.05$ – 0.25). The pore size distribution was derived from the desorption branch of the N_2 isotherm using the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of ca. 0.99. The diffuse reflectance UV–vis spectra were collected using a HITACHI UV3000 scanning spectrophotometer. The powder sample was loaded into a quartz cell, and the spectra were collected over the range of 200–800 nm reference to $BaSO_4$. Infrared spectra were recorded on a Bruker Tensor 27 using DRIFT techniques, scanned from 4000 cm^{-1} to 400 cm^{-1} . The sample was ground with KBr and pressed into a thin wafer. The ICP-AES was used to determine the content of lanthanide in the synthesized samples, which was performed on an OPTIMA 2000. Before any measurements were taken, the solid sample was dissolved in dilute HCl solution with a small amount of HF.

2.3. Catalytic activity investigation

Catalytic activity measurement was performed in a continuous flow fixed-bed reactor of 6 mm ID that was placed

in a tubular electrical furnace equipped with a temperature programmer. In each test run, 50 mg of catalyst diluted with an appropriate amount of inert quartz beads (40–60 mesh) was placed at the center of the reactor, above which a thermocouple was located to monitor the reaction temperatures. To create the steam containing benzene, one stream of pure air was passed through a boat-shaped saturator in an ice bath to produce a mixed gas containing benzene of high concentration, which was further diluted, with another stream of pure air before reaching the reaction bed. The total flow rate was set to be 320 ml min^{-1} with a concentration of ca. 1000 ppm by adjusting the two flow rates. The gas hourly space velocity (GHSV) in the tests was kept ca. 100000 h^{-1} . An on-line gas chromatograph equipped with a FID detector was used to analyze the concentration of benzene in the inlet and outlet gas. Before each measurement was taken, the temperature of the catalytic bed was raised to 120°C under the feed stream and stabilized at that temperature until the concentration of benzene became constant. No conversion of benzene was observed at this temperature. Then the temperature of catalyst bed was raised using a heating rate of 5°C/min , and the temperature was kept constant for 2 min at each datum point for equilibrium prior to analyzing the benzene concentration of the outlet gas.

3. Results and discussion

3.1. Effect of pH value

The acidic environment (pH value) of the whole synthesis procedure was variable and influenced by some factors

such as the protonation of the surfactant and the hydrolysis of the metal salt [7]. The changes in pH in the whole sol-gel procedure for the synthesis of La-SBA-15 (La/Si = 0.05–0.2) are shown in Table 1. Owing to the protonation of surfactant, the initial pH value of HCl solution was significantly increased to a higher value (pH^a) after the addition of the surfactant. However, after lanthanum nitrate was added, the pH^a value decreased again to a relative lower value (pH^b) due to the hydrolysis of the metal salt. For samples with initial pH <3.0, the pH^b was almost equal to the initial pH value of HCl, and the increase in the La/Si molar ratios slightly influenced the value of pH^b . When the initial pH value was 4.0 or 5.0, the pH^b was observed to be about 3.4. In order to objectively investigate the effect of pH on the synthesis of Ln-SBA-15, the pH^b of the above two cases was further adjusted with NaOH to 4.0 and 5.0 to keep consistent with their initial pH values. Fig. 1a shows the XRD patterns of La-SBA-15 (La/Si = 0.1) synthesized at different pH values. When the initial pH value is 1.5–3.0, La-SBA-15 samples display three well-resolved diffraction peaks, which are typical of the SBA-15 mesoporous materials. Compared with La-SBA-15 synthesized at initial pH <3.0, La-SBA-15 synthesized at pH^b 3.4 has poor quality with only one diffraction peak (100) in its XRD patterns (which are not shown in Fig. 1a). When the pH^b is 4.0 and 5.0, no characteristics peaks can be observed. As it can be seen in Table 1, there exists a relationship between the unit-cell parameter a_0 and the initial pH, i.e. with an increase in the a_0 values there is an increase in the initial pH, with a fixed La/Si molar ratio. For example, an increase in the initial pH from 1.5 to 3.0, the unit-cell a_0 of La-SBA-15 yielded in La/Si = 0.1 augments from 10.1 nm to 12.1 nm, as evidenced by the shift of peak (100) to lower 2θ values shown in Fig. 1. While the change of the La/Si molar ratios has no obvious effect on the unit-cell parameter a_0 , at the same the initial pH does, which can be identified in Fig. 2 and Table 2. The results in Table 1 also show that the content of La in the solid sample measured by ICP-AES is obviously lower than that in the gel. This indicates that the lanthanide species in the gel cannot be introduced completely into SBA-15 under weak acidic conditions. However, the content of La in the solid sample increases with the initial pH from 1.5 to 5.0. This shows that an increase in the initial pH favors the introduction of more La into SBA-15. But La-SBA-15 with ordered 2D hexagonal structure can only be obtained when the initial pH value is between 1.5 and 3.0.

Fig. 1b and c shows the XRD patterns of Ce-SBA-15 and Nd-SBA-15 with a constant Ce/Si and Nd/Si molar ratio of 0.1 synthesized under different acidic conditions (pH 1.5–3.0). As with La-SBA-15, all Ce-SBA-15 and Nd-SBA-15 samples have typical highly ordered hexagonal structure, indicating that the addition of Ce and Nd atoms into SBA-15 does not destroy the characteristic structure of SBA-15. It has also been found that with an increase in the initial pH, the 2θ peak (100) shifts to a lower value as observed in La-SBA-15.

Table 1
pH changes during the whole preparation procedure of La-SBA-15

Sample no.	Initial pH	(La/Si) _{gel} (%)	pH^a	pH^b	d_{100} (nm)	a_0 (nm)	(La/Si) _{solid} ^c (%)
1	1.5	5	3.05	1.54	9.5	10.9	0.52
2		10	3.05	1.55	8.7	10.1	0.64
3		15	3.06	1.52	9.5	10.9	0.71
4		20	3.05	1.54	9.6	11.1	0.85
5	2.0	5	3.24	1.92	10.6	11.2	0.58
6		10	3.26	1.90	9.9	11.5	0.69
7		15	3.30	1.91	9.9	11.4	0.75
8		20	3.22	1.89	9.7	11.2	0.84
9	2.5	5	3.92	2.56	10.5	12.1	1.23
10		10	3.96	2.54	10.3	11.9	2.82
11		15	3.91	2.48	10.5	12.1	3.12
12		20	3.92	2.48	10.5	12.1	4.22
13	3.0	5	4.51	3.05	10.3	12.0	1.85
14		10	4.51	3.02	10.5	12.1	3.01
15		15	4.54	3.02	10.6	12.2	4.76
16		20	4.39	3.01	10.5	12.1	5.23
17	4.0	10	5.36	3.35	–	–	–
18	5.0	10	6.42	3.38	–	–	–

^a The pH value of HCl-surfactant aqueous solution.

^b The pH value of mixed solution after the addition of metal salt.

^c La/Si (molar ratio) obtained by the ICP analysis.

Fig. 1. XRD patterns of Ln-SBA-15 samples synthesized at different pH with Ln/Si = 0.1: (a) La-SBA-15; (b) Ce-SBA-15 and (c) Nd-SBA-15.

The pH value is a decisive parameter in the synthesis of metal substituted SBA-15. When the acidity of the synthesis mixture is higher than the isoelectric point of silica (pH 2.0), the interaction mechanism between the polymer

Fig. 2. XRD patterns of Ln-SBA-15 samples with different Ln/Si molar ratios synthesized at pH 2.5: (a) La-SBA-15; (b) Ce-SBA-15 and (c) Nd-SBA-15.

micelle and the silica may be denoted as $S^0H^+X^-I^+$ type, where S^0 is the non-ionic surfactant, I^+ is the protonated silicon group and X^- is the Cl^- supported by HCl. When

Table 2
Physicochemical properties of Si-SBA-15 and Ln-SBA-15 Materials synthesized at pH 2.5

Sample	(Ln/Si) input (%)	(Ln/Si) ^a Output (%)	Total S_{BET}^b (m ² /g)	Mesopore S_{BET} (m ² /g)	Micropore S_{BET} (m ² /g)	Total D_V^c (cm ³ /g)	Micropore D_V (cm ³ /g)	D_P^d (nm)	a_0^e (nm)	W^f (nm)
SBA-15	–	–	362	275	87	1.1	0.07	7.05	10.5	3.5
La-SBA-15	5	1.23	798	574	224	1.1	0.12	6.4	12.1	5.7
La-SBA-15	10	2.82	865	584	281	1.1	0.13	6.2	11.9	5.7
La-SBA-15	15	3.12	823	549	274	1.2	0.11	6.5	12.1	5.6
La-SBA-15	20	4.22	835	580	255	1.1	0.12	6.6	12.1	5.5
Ce-SBA-15	5	1.42	894	643	251	1.2	0.11	6.6	11.8	5.2
Ce-SBA-15	10	3.05	925	660	265	1.2	0.12	6.5	12.1	5.6
Ce-SBA-15	15	3.78	864	630	234	1.2	0.11	6.5	12.1	5.6
Ce-SBA-15	20	4.21	861	596	215	1.2	0.10	6.6	11.9	5.3
Nd-SBA-15	5	1.22	900	633	267	1.2	0.12	6.4	11.7	5.3
Nd-SBA-15	10	2.95	857	603	254	1.2	0.12	6.6	11.7	5.1
Nd-SBA-15	15	3.24	889	625	274	1.2	0.12	6.2	11.3	5.1
Nd-SBA-15	20	4.15	850	597	253	1.1	0.12	6.6	11.5	4.9

^a Ln/Si (molar ratio) obtained by the ICP analysis.

^b BET specific surface area.

^c Total pore volumes were obtained at $P/P_0 = 0.99$.

^d BJH pore diameter calculated from the desorption branch.

^e a_0 calculated by d_{100} , $a_0 = 2 \times d_{100}/\sqrt{3}$.

^f Wall thickness = $a_0 - D_p$.

the acidity of the synthesis mixture is higher than the isoelectric point of silica, the interaction mechanism should be the $\text{S}^0\text{H}^+\text{I}^-$ type. When the initial pH < 3.0, inorganic species interact with protonated surfactant (P123) through the above two mechanisms. Large amounts of inorganic species aggregates around the polymer micelle. As a result, the concentration of inorganic species at the interface between the micelle and the solution is higher than that in solution, which facilitates further polymerization of inorganic species. According to cooperative formation mechanism [18], the polymerization of inorganic species can promote the formation of an ordered micelle crystal phase. When the initial pH > 3.0, the interaction between the surfactant and inorganic species becomes weak, thus inhibiting the polymerization of inorganic species. Consequently, the low degree of polymerization leads to the formation of an orderless micelle crystal phase.

3.2. Effect of Ln/Si ratio

Fig. 2 shows the XRD patterns of the Ln-SBA-15 samples with different Ln (La, Ce, Nd)/Si molar ratios synthesized at pH 2.5. Three well-resolved diffraction peaks of all the samples, indexed as the (100), (110), (200) diffractions, reflect the two-dimensional hexagonal mesostructure with a space group of $p6mm$ symmetry. With different heterogeneous atoms (La, Ce, Nd), the 2θ values of peak (100) shift to a lower value compared with that of pure SBA-15, indicating that the unit-cell a_0 ($a_0 = 2d_{100}/\sqrt{3}$) increases after the incorporation of the lanthanide ions. As others have previously reported [15,19], the lengths of Ce–O and La–O bonds are larger than that of Si–O bond, thus their incorporation into the framework of MCM-41 may increase the unit-cell parameter a_0 . Other scientists have also reported similar observations with different metal ions

incorporated into SBA-15 [20]. Hence, we can infer that the lanthanide ions (La, Ce, Nd) have been incorporated into the framework of SBA-15. Moreover, the intensities of the XRD peaks of Ln-SBA-15 materials are greater than that of the pure silica SBA-15 sample, which may be attributed to the catalysis of the nitrate ions (from the Ln source) to the condensation of silica species that can assist the formation of a well-ordered structure [21,22]. However, the long-range ordering of Ce-SBA-15 and Nd-SBA-15 is gradually lost with an increase in Ce/Si and Nd/Si molar ratios. This may be due to an increasing number of defect sites and bond strain of these materials that is evidenced by the decreasing intensities of the (100) peak [15].

The structural properties of Ln-SBA-15 were measured by N_2 sorption. Here Ce-SBA-15 synthesized with different Ce/Si ratios at pH 2.5 are taken as examples and their nitrogen sorption isotherms and pore size distributions are given in Figs. 3a and 3b. A peculiar two-step behavior is observed on the hysteresis loop of all the Ce-SBA-15 samples with Ce/Si = 0.02–0.2 presented in Fig. 3a. The empty mesopores behave like cylindrical mesopores with a hysteresis loop at higher relative pressures ($P/P_0 = 0.6$) [23], whereas the mesopores with cerium oxide particles inside behave like ink bottle type mesopores with a hysteresis loop that closes around at a relative pressure of ca. 0.4. The hysteresis loop at ca. 0.4 can still be explained by the fact that SBA-15 contains micropores [24]. The textural properties of Ln-SBA-15 and pure SBA-15 are shown in Table 2. All the Ln-SBA-15 samples synthesized at pH 2.5 have relatively higher specific surface area (798–925 m²/g) than pure SBA-15 synthesized at the same condition (362 m²/g), which is essentially due to the larger mesopore S_{BET} of Ln-SBA-15 samples (549–660 m²/g) than that of pure SBA-15 (275 m²/g). This may be ascribed to the enhancement in the long-range ordering of the mate-

Fig. 3a. Nitrogen adsorption-desorption isotherm of Ce-SBA-15 samples synthesized at pH 2.5 with different Ce/Si molar ratio: (a) Ce/Si = 0.02; (b) Ce/Si = 0.05; (c) Ce/Si = 0.1 and (d) Ce/Si = 0.2.

Fig. 3b. Pore size distribution of Ce-SBA-15 samples synthesized at pH 2.5 with different Ce/Si molar ratio: (a) Ce/Si = 0.02; (b) Ce/Si = 0.05; (c) Ce/Si = 0.1 and (d) Ce/Si = 0.2.

rials induced by the salt effect after the addition of the Ln precursor. Compared with pure SBA-15, the pore volumes of Ln-samples reduce slightly, whereas the pore diameters of Ln-SBA-15 samples decrease from 7.0 nm to ~6.2 nm. Hence, Ln-SBA-15 materials have a larger wall thickness because they have larger a_0 values calculated from above XRD results. For all the Ln-SBA-15 materials, it seems that the variation of the Ln/Si molar ratios from 0.05 to 0.2 have little influence on the pore size and pore volume.

Since SBA-15 is typically known to have considerable micropores that originate from the corona of the silica wall, it will be interesting to observe the changes of the micropore structure after the incorporation of Ln ions in the silica matrix. Under normal conditions of preparation of SBA-15 (pH < 0), the micropore volume is reported to be about 5–8% of the overall pore volume [24]. While under present condition (pH 2.5), the contribution of microporosity to the total pore structure is increased to 6–12%. Under mild acidic conditions, the rate of condensation is faster than the rate of hydrolysis of TEOS and therefore a larger number of micropores is generated in SBA-15 samples. Furthermore, the micropore S_{BET} and D_V of Ln-SBA-15 are relatively higher than that of pure SBA-15, which confirms that the addition of lanthanide directly influences the microporous structure in framework.

3.3. Coordination environment of lanthanide

Fig. 4 shows the diffuse reflectance UV-vis spectra of the Ce-SBA-15 sample synthesized at pH 2.5 with Ce/Si = 0.1. For comparison purposes, the UV-vis spectra of the impregnated Ce-Im-SBA-15 (Ce/Si = 0.03) and pure CeO₂ samples are also shown in Fig. 4. The two maximum adsorption peaks produced by the unsupported ceria can be credited to the specular reflectance which affects the shape of the interband transition, although not modifying the absorption peak position which appears at ca. 400 nm [25]. In the case of the Ce-SBA-15 and Ce-Im-SBA-15 samples, the adsorption peak shifts to 300 nm and 280 nm, respectively. Other scientists have also observed these two peaks and have provided their interpretation in regards to this phenomenon. In Li's study, the absorption band centered at 300 nm was attributed to the metal charge

Fig. 4. Diffuse reflectance UV-vis adsorption spectra of samples: (a) CeO₂; (b) Ce-Im-SBA-15 (Ce/Si = 0.03) and (c) Ce-SBA-15.

transfer ($O^{2-} \rightarrow Ce^{4+}$) of CeO_2 clusters of several nanometers in size [26]. Laha characterized Ce-MCM-41 with UV–vis spectra and made a conjecture that the adsorption peak at 300 nm was due to the presence of one type of well-dispersed Ce^{4+} species (presumably in a tetra-coordinated environment) [15]. Bensalem ascribed the adsorption band centered at 280 nm to the Ce^{4+} -oxygen charge transfer transitions predominating in the presence of small crystallites [27]. For all the samples in our study, a weak absorption band centered at 210 nm was observed, which can be credited to the 4f–5d inter-configuration transition of the Ce^{3+} species [26]. Based on the above interpretation made by Laha on the adsorption peak at 300 nm, we cannot make a conclusive statement about the coordination state of the Ce^{4+} ion in the Ce-SBA-15 materials. At least we can infer that most of the Ce^{4+} are highly dispersed in Ce-SBA-15 from the wide-angle XRD spectrum of Ce-SBA-15 (Ce/Si = 0.1, synthesized at pH 2.5) shown in Fig. 5. This is due to the intensities of the CeO_2 peaks of Ce-SBA-15 being weaker than those of Ce-Im-SBA-15 (Ce/Si = 0.03) synthesized by the impregnation method, although they were synthesized using the same Ce/Si molar ratios. Thus, it can be concluded that there exist large amounts of well-dispersed isolated Ce^{4+} in the framework of the Ce-SBA-15 sample, or there exist cerium species in the nanometer scale that are too small to have diffraction peaks.

The FT-IR spectra of pure SBA-15 and different Ln-SBA-15 samples are shown in Fig. 6. In the framework region (400–1300 nm), the vibration band at ca. 1082 cm^{-1} (for pure SBA-15) is assigned to $\nu_{as}(\text{Si-O-Si})$, while for Ln-SBA-15, this band shifts toward the lower wave number ca. 1064 cm^{-1} . Generally speaking, this shift toward the lower wave number is considered as an indication of the incorporation of Ln ions into the framework of

Fig. 5. XRD patterns of Ce-Im-SBA-15 (Ce/Si = 0.03) (a) and Ce-SBA-15 (Ce/Si = 0.1) synthesized at pH 2.5 (b).

Fig. 6. FT-IR spectra of Si-SBA-15 and Ln-SBA-15 (Ln/Si = 0.1) synthesized at pH 2.5: (a) Si-SBA-15; (b) La-SBA-15; (c) Ce-SBA-15 and (d) Nd-SBA-15.

SBA-15 [15]. For Ln-SBA-15, the band at ca. 960 cm^{-1} can be assigned to a $\nu_{as}(\text{Si-O-Ln})$ vibration present in the framework of SBA-15 [15]. However, a band at ca. 965 cm^{-1} is also observed in the pure SBA-15. This band can be assigned to the Si-O stretching vibrations of the Si-O-R^+ groups, as $\text{R}^+ = \text{H}^+$ groups are present in the calcined state [28]. Therefore, this band cannot be taken as proof of Ln incorporation in the framework of SBA-15 because a large number of silanol groups are always present in Si-SBA-15. It is also observed that the $\nu_{as}(\text{Si-O-Ln})$ and/or $\nu(\text{Si-OH})$ band intensity increases with respect

Fig. 7. Benzene conversion on Pd catalysts over Ln-containing supports with Ln/Si = 0.1 (▼) Pd/Nd-SBA-15; (◆) Pd/La-SBA-15; (▲) Pd/Ce-SBA-15; (■) Pd/Ce-Im-SBA-15 and no Ln-containing supports (●) Pd/SBA-15 (★) Pd/ $\gamma\text{-Al}_2\text{O}_3$.

Table 3
Activity data of the samples in the catalytic oxidation of benzene

Samples	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
Pd/ γ -Al ₂ O ₃ ^a	250	267	288
Pd/Ce-Im-SBA-15 ^b	241	257	324
Pd/SBA-15 ^c	201	218	246
Pd/La-SBA-15	192	212	229
Pd/Ce-SBA-15	193	216	239
Pd/Nd-SBA-15	192	204	219

^a γ -Al₂O₃ is a Commercial product.

^{b,c} Ce-Im-SBA-15 was Ce impregnated Im-SBA-15 with Ce/Si = 0.03.

to that of $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ and/or $\nu(\text{Si}-\text{OH})$ band when Ln are incorporated. This may be taken as an evidence of the incorporation of the Ln metal into the framework of mesoporous materials. In all spectra, the band at ca. 800 cm⁻¹ is assigned to the symmetric Si–O–Si stretching vibration [29–31]. In the hydroxyl region (3000–4000 cm⁻¹), the adsorption band at 3420 cm⁻¹ for all the samples is attributed to the stretching vibrations of the silanol groups interacting via hydrogen bonding [32].

3.4. Catalytic activity

The catalytic oxidation of benzene was carried out using different Pd/Ln-SBA-15 samples. For comparison reasons, Pd/SBA-15, Pd/Ce-Im-SBA-15 and Pd/ γ -Al₂O₃ were also used to measure their catalytic activities. The results are shown in Fig. 7. It is observed that Ln-SBA-15 supported Pd catalysts show higher catalytic activities than SBA-15, γ -Al₂O₃ and Ce-Im-SBA-15 supported Pd catalysts. The activity data of the catalysts tested are listed in Table 3. Among the catalysts, Pd/Nd-SBA-15 shows the best catalytic performance, for which 90% oxidation of benzene is achieved at 219 °C. Although the value of T_{10} (the temperature at which the benzene conversion reached 10%) is similar for Pd/Ln-SBA-15 in the reaction, T_{90} (the temperature at which the benzene conversion reached 90%) for Pd/La-SBA-15 and Pd/Ce-SBA-15 is 229 °C and 239 °C respectively, which is lower than that of Pd/Nd-SBA-15. T_{90} for Pd/SBA-15 is about 250 °C and 100% oxidation of benzene is achieved at 300 °C. Whereas for Pd/Ln-SBA-15, the temperatures at which benzene are completely converted are found at about 260 °C. This decrease of T_{100} can be attributed to the incorporation of lanthanide into SBA-15, which is seen as an advantage as it enhances the catalytic activity of catalysts. The importance of lanthanide in promoting oxidation reactions of VOCs has been previously reported [33–36]. As shown in Fig. 7, the 100% conversion of benzene for Pd/ γ -Al₂O₃ and Pd/Ce-Im-SBA-15 was obtained at 400 °C, with T_{10} of 250 °C and 240 °C respectively. It should be noted that the Pd/Ce-Im-SBA-15 shows the poorest performance in the catalytic oxidation of benzene from 270 °C to 400 °C. The activity of Ceria-based catalyst is known to strongly depend on its structure. Nanosized ceria shows higher activity than that of bulk-phase ceria, because of the easier reduction of the

surface oxygen species on ceria nanoparticles [37,38]. Thus, it can be concluded that Ce-SBA-15 synthesized in this work shows better activity than Ce-Im-SBA-15 as a catalyst support which is probably due to the presence of large amounts of well-dispersed Ce⁴⁺ species in the Ce-SBA-15 material, as previously discussed in Section 3.3.

4. Conclusions

In summary, lanthanide-containing SBA-15 materials La-SBA-15, Ce-SBA-15 and Nd-SBA-15 materials have been successfully synthesized using a direct synthesis method under weak acidic conditions. The initial pH of the HCl solution plays an important role in the preparation of well-dispersed and ordered Ln-containing SBA-15 materials and must be strictly controlled between 1.5 and 3.0. The addition of Lanthanide nitrate also favors the ordering of the mesoporous structure of the materials due to their salt effect. In the catalytic characterization, the Ln-SBA-15 supported Pd catalysts show higher catalytic activity than other catalysts prepared in our laboratory by the impregnation method, which is notably higher than that of Pd/Ce-Im-SBA-15. It further testifies the advantage of using the direct synthesis method in the preparation of highly dispersed heteroatom-containing materials. This type of Ln-SBA-15 materials shows great potential as support in the catalytic reactions, such as in the catalytic oxidation of VOCs originated from industrial emissions.

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