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Research Paper

Preparation and characterization of lanthanum phosphate catalysts for *O*-methylation of phenol to anisole in gas phase

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ABSTRACT

Lanthanum phosphate catalysts have been synthesized in 3 different techniques such as (i) simple co-precipitation (LaP-1), (ii) co-precipitation followed by hydrothermal treatment (LaP-2) and (iii) pH variation method (6LaP-3 the prefixed 6 denotes the flocculated pH). Lanthanum and phosphate concentration in all the catalysts is constant (La/P = 1) irrespective of method of preparation. All the 3 catalysts (LaP-1, LaP-2 and 6LaP-3) prepared by different methods are used as catalysts for the *O*-methylation of phenol and found that the catalyst prepared by pH variation method (6LaP-3) exhibited better activity. A series of catalysts with La/P = 1 by pH variation method (2LaP-3, 6LaP-3, 9LaP-3 and 12LaP-3) have been prepared and characterized by FT-IR, X-ray diffraction and BET surface area to obtain the structural and textural information. Temperature programmed desorption of NH_3 and CO_2 studies of LaP-3 catalysts revealed the distribution and strength of acidic and basic sites respectively. LaP-3 catalysts are in hexagonal and rhabdophane phases (XRD). The LaP-3 catalysts are highly active and selective towards formation of anisole via methylation of phenol with methanol in the vapor phase. 2LaP-3 is the best catalyst among the LaP-3 catalyst series in the catalytic activity point of view. Weak and moderate acidic sites along with basic sites might have contributed for the high conversion of phenol and good selectivity of anisole.

1. Introduction

Production of anisole by selective *O*-methylation of phenol with methanol is an industrially important reaction because of its alluring industrial applications. Anisole is extensively used in the production of perfumes, insect pheromones, phenol-formaldehyde resins, pharmaceuticals, cosmetics [1–4] and also an important chemical intermediate for synthesizing guaiacol, MEHQ (Mono methyl ether of hydroxyl quinine) and 4-MAP (4-Methoxy acetophenone). Besides, it is utilized in the manufacture of nanoparticles and inorganic complexes. Commercially anisole being produced by based on the Williamson's ether synthesis wherein phenol, methyl bromide and alkaline sodium compounds are used. Traditionally, for the synthesis of anisole Friedel–Crafts catalysts such as $AlCl_3$, BF_3, $TiCl_4$ and liquid HF are being utilized. However, disposal of effluents, corrosiveness, low reaction selectivity, catalyst separation, toxicity etc, are hurdles for the practical utility of this technology. Another anisole manufacture process is from phenol and dimethyl ethere with dehydrating catalyst in vapor phase. But this possess suffers from low selectivity and fast deactivation of the catalysts. Conventional methylating agents, such as methyl chloride and dimethyl sulfates are currently less attractive due to environmental concerns [5,6]. Therefore methanol has been emerging as eco-friendly methylating agent [7]. Recently, much attention has been paid on the eco-friendly catalysts to replace the mineral acid catalysts. In the recent past, *O*-methylation of phenol with methanol in vapor phase has been reported using clays, mixed metal oxides, sulfated metal oxides, zeolites, etc [8–14] as catalysts. Though the methylation of phenol is the subject interest for several authors, no clear cut understanding in the case of acid-base properties of the catalysts. According to some reports, catalysts with strong acidic sites favor *O*-methylation, weak acidic or strong basic sites favor the *C*-methylation [11,12,15–17]. Contrarily, catalysts with weak acidic sites favor *O*-methylation of phenol [18,19]. Of late, methylation of phenol with methanol as methylating agent over metal phosphates catalysts has been investigated and reported that the products are less selective towards *O*-methylation, i.e., yielding the mixture of *O*-methylated and *C*-methylated products [20,21]. In recent times, much attention has been paid on synthesis, characterization and catalytic applications

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of lanthanum phosphate catalysts based on their acid-base bifunctional characteristics and vital catalytic properties.

In the present study, aiming at understanding the relation between acid-base characteristics and product selectivity in methylation of phenol, lanthanum phosphate catalysts by different methods keeping lanthanum to phosphate ratio constant at 1 (La/P = 1) three catalysts were prepared by (i) simple co-precipitation method (LaP-1), (ii) co-precipitation followed by hydrothermal treatments (LaP-2) and (iii) co-precipitation by pH variation method (6LaP-3). In the catalytic activity point of view, the catalyst prepared by pH variation method exhibited superior activity. Hence, three more lanthanum phosphate catalysts apart from 6LaP-3 were prepared by pH variation method at pH = 2, 9, and 12 and denoted as 2LaP-3, 9LaP-3 and 12LaP-3 catalysts.

Herein, the details of lanthanum phosphate catalyst preparation (pH variation), characterization and catalytic activity for the selective *O*-methylation of phenol emphasizing the acid-base properties have been delineated for the first time.

2. Experimental

2.1. Catalyst preparation

Lanthanum phosphate catalysts at constant lanthanum to phosphate ratio (La/P = 1) were prepared by different methods such as (i) simple co-precipitation, (ii) co-precipitation followed by hydrothermal and (iii) co-precipitation by pH variation.

2.1.1. Simple co-precipitation method

Lanthanum phosphate catalyst (La/P = 1) was prepared according to reported method [22] and denoted as LaP-1 catalyst. Typically, 6.234 g of La $(NO_3)_3 \cdot 6H_2O$ dissolved in 480 mL of distilled water and added 1.41 g of H_3PO_4 drop wise. The pH of formed white gel was adjusted to 8 with 25% ammonia solution under continuous stirring for 24 h at RT. The precipitate was separated by filtration and washed with distilled water, dried at 100 °C for 24 h and calcined at 400 °C for 4 h in static air.

2.1.2. Co-precipitation followed by hydrothermal treatment

According to reported procedure lanthanum phosphate [23] catalyst was prepared and designated as LaP-2. Typically, 25 mL of 0.8 M aqueous solution of La $(NO_3)_3 \cdot 6H_2O$ and the same concentration of Na_3PO_4 were prepared separately and added at once under vigorous stirring for 30 min pH was adjusted <1 with 0.1 M HCl under stirring. Subsequently, Pluronic P123 polymer was added to the suspension under stirring at 40 °C, and continued the stirring for 2 h, transferred to autoclave, hydrothermally treated at 100 °C. Precipitate was filtered and washed with distilled water. The resulting solid sample was calcined at 550 °C for 6 h to remove the P123 polymer.

2.1.3. Co-precipitation by pH variation method

Lanthanum phosphate catalyst was prepared in accordance with the reported literature report [24] and coded as La*P*-3. In a typical procedure, 0.03 M aqueous solution of La $(NO_3)_3 \cdot 6H_2O$ solution was prepared. While stirring at RT H_3PO_4 (1.41 g) (La/P = 1) was added drop wise to the lanthanum nitrate solution. A white gel like precipitate of lanthanum phosphate was formed, which was completely flocculated with 25% ammonium solution at a pH of 6, then filtered and washed with distilled water. Filtered precipitate was peptized under stirring for 4 h at RT by adding 20% (v/v) HNO_3 to maintain the pH range in between 1.8–2. Then centrifuged the peptized milky white solution and washed with distilled water. The washed sample dried at 80 °C for 12 h, calcined at 400 °C for 4 h (ramping rate 10 °C/min) in static air. The calcined sample was coded as 6LaP-3, wherein 6 represents the flocculated pH value and 3 refers to adopted preparation method. Following the similar procedure 2LaP-3, 9LaP-3 and 12LaP-3 catalysts were synthesized.

2.2. Catalyst characterization

The lanthanum phosphate samples were analyzed by elemental analysis (ICP-OES M/s. Thermo Scientific iCAP6500 DU) by dissolving in aquaregia along with few drops of hydrofluoric acid. XRD patterns were recorded on an Ultima-IV (M/s. Rigaku Corporation, Japan) XRD unit operated at 40 kV and 40 mA with nickel-filtered Cu Kα radiation. The BET surface area was determined by N_2 physisorption (M/s. Quantachrome Instruments, USA). Temperature programmed desorption of ammonia (TPD – NH_3) was measured by AUTOSORB-iQ, automated gas sorption analyzer (M/s. Quantachrome Instruments, USA). Prior to desorption, the catalyst samples have been saturated with the ammonia (10% NH_3 balance helium) at 80 °C for 30 min, followed by removal of the physisorbed NH_3 through the stripping with helium at the same temperature for 30 min. Later on, the temperature was raised to 800 °C at the rate of 10 °C/min, with simultaneous monitoring of the desorbed NH_3 with the inbuilt TCD in a flow of helium (60 mL/min). The TPD of CO_2 was conducted similar to that of TPD of NH_3, with just replacing NH_3 by CO_2 (10% CO_2 balance helium). FT-IR spectra were recorded on a spectrum GX spectrometer (M/s. Perkin-Elmer, Germany) in the scan range of 4000–400 cm^{-1} with the 4 cm^{-1} spectral resolution using KBr disc method.

2.3. Activity test

Activity tests were conducted in a fixed-bed down flow quartz glass reactor (14 mm id and 300 mm long). 1.0 g of the catalyst and equal amount of the quartz particles were mixed and loaded at the centre of the reactor and flushed at 400 °C for 1 h in N_2 flow of 30 mL/min. Silicon beads were used as preheating zone. With 3 mL/h feed (phenol: methanol = 1: 9, v/v) using a syringe pump (M/s. B. Braun, Germany) run the reaction. The product mixture was collected in an ice cooled trap at regular intervals and analyzed by a FID equipped GC (GC-17A, M/s. Shimadzu Instruments, Japan) with Suplecowax capillary column (30 m × 0.53 mm × 5.0 μ m) and products were confirmed by GC–MS, QP-5050 (M/s. Shimadzu Instruments, Japan) with DB–5 capillary column (30 m × 0.25 mm × 0.25 μm). The reactor diameter is 14 mm and bed length is around 0.5 mm. Hence, either diffusion limitations or mass transfer limitations may not be substantial influence.

3. Results and discussion

3.1. Characterization of catalysts

According to ICP-OES analysis lanthanum to phosphate ratio is around 0.98–0.99, which is close to amount of precursors used. The BET surface areas of LaP-3 catalysts are presented in Table 1, which

Table 1
BET surface area and acid-base properties of LaP-3 catalysts.

Catalyst code	[a]Crystallite size (nm)	[b]S_{BET} (m^2/g)	[c]Total acidity (NH_3 mmol/g)	[d]Total basicity (CO_2 mmol/g)
2LaP-3	11	97	0.40	1.50
6LaP-3	12	94	0.45	1.35
9LaP-3	12	76	0.36	1.29
12LaP-3	12	71	0.30	1.24

[a] Obtained from Debye Scherrer equation.
[b] BET surface area from N_2 adsorption.
[c] Total acidity obtained from TPD of NH_3.
[d] Total basicity obtained from TPD of CO_2.