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Vapor-phase selective o-alkylation of catechol with methanol over lanthanum phosphate and its modified catalysts with Ti and Cs

Ali Abedi Jafari*, Abbasali Khodadadi, Yadollah Mortazavi

School of Chemical Engineering, University of Tehran, Tehran, Iran

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ABSTRACT

Vapor-phase o-alkylation of catechol with methanol over lanthanum phosphate catalyst is studied. Also, the effects of the reaction temperature and the weight hourly space velocity (WHSV) on the catalyst performance were evaluated. Expectedly, the catechol conversion and the guaiacol selectivity were inversely correlated as the secondary reactions proceeds further at higher guaiacol concentrations. Catalyst characterization indicated that the medium acidic sites played the major role in the conversion of catechol. Addition of titanium into lanthanum phosphate ($La_{1-x}Ti_xPO_4$, x varies from 0.0 to 0.5) increased the surface area and acidity of the catalyst whereas a dramatic decline in the number of acidic sites, BET surface area was observed when catalyst was impregnated with up to 10% cesium. The catechol conversion first increased by addition of small quantities of titanium after which it substantially decreased. However, the catalyst selectivity to guaiacol monotonically decreased by increasing the titanium loading on the catalyst. The highest guaiacol yield was obtained using $La_{0.9}Ti_{0.1}PO_4$ where a maximum in catalyst acidity per specific surface area was also observed (i.e. 0.336 μmol g/m^2). Moreover, a linear relation between the numbers of catalyst acid sites per surface area and the catechol conversion was observed.

1. Introduction

Recently, there has been a high demand to reduce the negative environmental impacts of chemical processes. High selectivity for the production of a desired product, and minimizing the side-products, has become increasingly significant, both for economical (less separation steps) and product quality purposes.

Heterogeneous catalysis can be utilized to meet those requirements because it allows the replacement of stochiometric reactants and may improve the reaction pathway leading to the formation of the desired product. The alkylation of phenol and polyhydroxybenzenes such as catechol on the oxygen atom (o-alkylation) for the synthesis of alkylarylethers is an example of an industrially important reaction that needs a proper alternative in order to produce higher-quality products [1].

The desired product in catechol alkylation is guaiacol. This product is produced when the reaction goes to o-alkylation pathway rather than c-alkylation. If o-alkylation continues further, another product which is veratrole may be produced. Since the separation of guaiacol and veratrole is an expensive process, o-alkylation should be controlled accurately. c-Alkylation products are 3- and 4-methyl catechol.

Guaiacol is an essential synthetic intermediate in fine chemical production. It is widely used for production of flavoring additives, fragrances, agricultural chemicals, and pharmaceuticals [2]. Traditionally, guaiacol is synthesized by alkylation of catechol with corrosive reagents like dimethyl sulfate and dimethyl iodide in the presence of stoichiometric quantities of sodium hydroxide as a homogeneous catalyst. Recently, vapor-phase alkylation of catechol for the synthesis of guaiacol in the presence of heterogeneous catalysts has received more attention [3].

The general alkylation agents include dimethyl carbonate (DMC) and methanol. A few catalysts such as Al_2O_3 [4], alkaline Al_2O_3-based [5–7], and Mg–Al hydrotalcite [8] have been employed for the reaction using DMC as the alkylation agent. In comparison with DMC, methanol is considered as the most suitable agent for practical applications due to its lower cost. Several heterogeneous catalysts have been tested in the vapor-phase alkylation of catechol with methanol, including BPO [1], AlPO [9], AlTiPO and AlTiSiPO [10], alkaline loaded silica [11], $ZnCl_2$ on Al_2O_3 [12], ammonium metatungstate impregnated SiO_2, TiO_2 and Al_2O_3 [13], and sulphate-modified zirconia [14].

Govic et al. [15] found that rare-earth phosphates including lanthanum phosphate could be used for selective o-alkylation of phenols including catechol.

Some authors proposed mechanisms based on the contribution of acid-base sites for some catalysts such as BPO, AlPO, AlTiPO, AlTiSiPO, and ammonium metatungstate impregnated SiO_2, TiO_2, and Al_2O_3.

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* Corresponding author. Tel.: +98 21 44040112; fax: +98 21 44040282.
E-mail address: aliabedijafari@gmail.com (A.A. Jafari).

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Some others proposed acidic mechanism for $ZnCl_2$ on Al_2O_3, sulphate-modified zirconia, alkaline loaded silica and rare earth phosphates specially $SmPO_4$.

Thus, there is no generally accepted mechanism. However, most of researches show that catechol alkylation needs mild acidity as reported by several authors [1,9,10,13,14].

In this research, we show that acidic sites are responsible for o-alkylation of catechol over $LaPO_4$. Addition of cesium and titanium can considerably affect the acidic property of the catalysts and their performance consequently.

2. Experimental

2.1. Catalyst preparation

Lanthanum phosphate was synthesized by the reaction of lanthanum nitrate and phosphoric acid. Lanthanum nitrate dissolved in distilled water and phosphoric acid was added to the mixture drop wise (La/P = 1 mol). Lanthanum phosphate precipitated suddenly. The mixture was stirred using a magnetic stirrer for 6 h at 96 °C. The precipitated gel was filtered and washed with distilled water several times to assure that no excess acid or nitrate remained. The filtrate was dried overnight at 96 °C and calcined at 400 °C for 2 h.

Lanthanum phosphates with various amounts of cesium were prepared by impregnation method. The proper amount of cesium nitrate was dissolved in distilled water and cesium-lanthanum phosphate was prepared by impregnation method. Catalysts were dried overnight at 130 °C and calcined at 400 °C for 2 h.

The titanium containing lanthanum phosphate catalysts were prepared by ammonia gelation method. The proper amount of lanthanum nitrate was dissolved in distilled water. Lanthanum hydroxide was precipitated by addition of ammonia solution. The addition of ammonia was continued until the pH of the solution became 10. Afterwards, the tetraisopropyl orthotitanate was added into the slurry while stirring vigorously. Phosphoric acid was then added to the mixture gradually. The final mixture was stirred at 96 °C for about 6 h. The white powder was filtered and washed with distilled water several times until the pH of the aqueous phase in filtration step became 7. The powder was dried overnight at 130 °C and calcined at 600 °C for 2 h. By this method, we prepared the catalyst with a general formula of $La_{1-x}Ti_xP$ (x = 0.0, 0.10, 0.23, and 0.50).

2.2. Catalyst characterization

X-ray diffraction powder (XRD) was performed with a Philips diffractometer operated at 50 kV and 150 mA using nickel-filtered Cu Kα radiation.

BET surface area measurements and temperature-programmed desorption (TPD) experiments were accomplished using a CHEMBET 3000 (Quantrachrome). Before the experiment, the samples were pretreated under flow of pure nitrogen at 400 °C for about 1.5 h.

For the TPD experiments pyridine was used as the probe molecule. In a standard procedure, 100 mg of fresh sample was used. The sample was saturated with the probe molecule by several consecutive injections. Following the saturation, the system was purged with He for one hour. The sample was heated at the rate of 10 °C/min in a He flow of 17 stpml/min. Concentration of the desorbed pyridine was monitored.

Lanthanum and titanium content of the catalysts were measured by an inductivity coupled plasma apparatus, a Varian 150Ax Laboratory Turbo.

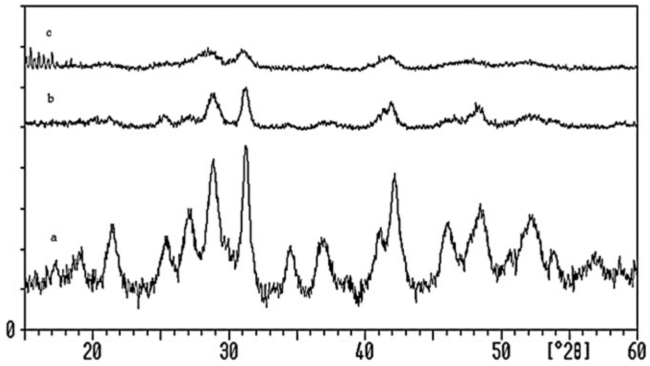

Fig. 1. XRD pattern of lanthanum phosphates. (a) $LaPO_4$, (b) 1% Cs-$LaPO_4$, and (c) 3% Cs-$LaPO_4$.

2.3. Catalytic tests

The vapor phase o-alkylation of catechol with methanol was carried out in a fixed bed continuous down-flow reactor at atmospheric pressure. Temperature of the reaction was controlled by a PID temperature controller. Prior to the reaction, the catalyst (0.8 g, 40–60 mesh) was activated in the glass-tube reactor (i.d. = 10 mm and length = 25 cm) at 500 °C for 1 h in a nitrogen flow. A pre-mixed catechol–methanol mixture was then fed from the top of the reactor by means of a Sage-Instrument syringe pump along with Ar (15 ml/min). The products were cooled in an ice-water bath condenser, collected in a receiver and analyzed in a gas chromatograph (Varian 3800; capillary column DB-5, 50 m × 0.2 mm; FID detector). The reaction conditions were as follows: catechol/methanol = 1/5 (mole ratio), reaction temperature = 255–300 °C, weight hourly space velocity (WHSV) = 2.2 h^{-1}.

3. Results and discussion

3.1. Lanthanum phosphate performance

The XRD patterns of $LaPO_4$ and Cs-$LaPO_4$ catalysts are presented in Fig. 1. The sample has three peaks covering the 2θ range of 28–32 and 40–45. This figure indicates that the crystalline lanthanum phosphate forms clearly with monoclinic phase.

In order to measure the molar ratio of La to P in $LaPO_4$, ICP measurements were performed. The ICP results revealed that this ratio was 0.98. The measured concentrations were generally comparable with the nominal amounts.

The BET surface area measurement of $LaPO_4$ indicated that the surface area of the lanthanum phosphate catalyst was fairly high (94 m^2/g).

Alkylation of catechol with methanol over lanthanum phosphate in the gas phase shows promising results. The reaction over this catalyst, as seen in Table 1, proceeds via the o-alkylation pathway. Catechol conversion reaches to 67.1% and 90.9% of catechol converts to guaiacol. Small amounts of veratrole and c-alkylation products (3 and 4 methyl catechol) were detected.

Table 1
Effect of temperature on lanthanum phosphate activity.

Temperature (°C)	Catechol conversion	Selectivity		
		Guaiacol	Veratrole	c-Alkylation
255	67.1	90.9	6.5	2.6
275	75.2	79.9	14.7	5.4
300	84.3	63.6	25.6	10.8

Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h^{-1}.