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Enhanced Performance in Vapor O-Methylation of Hydroxybenzene Over a Noval Kind of Mesoporous Rare Earth Phosphate

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Mesoporous rare earth phosphates (MREPs) have been prepared by template method. The mesoporous structure of these materials has been characterized by XRD and TEM measurement. The catalytic performance of these materials in vapor O-methylation of hydroxybenzene has been investigated. These MREPs show higher performance in O-methylation of hydroxybenzene than the materials prepared without template. The excellent performance of these MREPs could be ascribed to their porous structure and much more amount of active sites.

1. Introduction

Porous materials have some good characters, such as high surface area, controllable adsorption properties and designable morphologies, thus, porous material are potential candidates for catalysis, adsorption and hosts of nanomaterial synthesis, etc[1]. For mesoporous materials, they possess larger channels(2~50 nm) than zeolites, holding more promise for the catalytic application to the direct activation of large organic molecule or for supporting active sites bearing large organic functionalities[2]. In recent years, much attention has been devoted to the synthesis and characterization of rare earth phosphates, because of their practical or

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potential applications in optical materials (including laser, phosphors, anti-UV materials), sensors, ceramic materials, heat-resistant materials and catalysis materials, etc[3–13]. For these reasons, it is anticipated to the synthesis and application of mesoporous rare earth phosphates(MREPs). However, to our knowledge, there is still little research in mesoporous rare earth phosphates, which might be caused by the reasons that the prepared mesoporous rare earth phosphates are thermally unstable, or the application of mesoporous rare earth phosphates is still limited.

O-alkylation of hydroxybenzene is a series of reactions, such as O-alkylation of phenol with methanol for the synthesis of anisole, O-alkylation of catechol with methanol for the synthesis of guaiacol, etc. The products of O-alkylation reactions, such as anisole and guaiacol, are important intermediates in the fields of flavouring agents, fragrances, dye, agricultural chemicals and pharmaceuticals[14, 15]. Traditionally, these kinds of products were synthesized by Williamson ether synthesis, which require corrosive reagents such as dimethyl sulfate or alkyl halide in the presence of stoichometric amount of sodium hydroxide as the homogeneous catalyst[16]. The use of corrosive reagents and homogeneous catalyst will cause environmental problems and produce a large amount of wastes. To overcome these problems, various solid catalysts have been used to finish this process, such as clays, heteropoly acids, sulphate-doped metal oxides, metal and mixed metal oxides, metal phosphates and zeolites, etc[16–31], since this route is more economical and more environmentally friendly for industrial applications. It was concluded that the strong acid catalysts favored ring alkylation, yet the weak acid or base catalysts can help O-alkylation[32]. However, the performance of solid catalysts is still not satisfactory for their low conversion and short lifetime.

In this study, a novel kind of rare earth phosphate with a mesoporous microstructure has been prepared by template method. Catalytic performance of this kind of rare earth phosphate in vapor O-methylation of hydroxybenzene has been investigated, and the effect of catalyst structure of these MREPs for the excellent performance has also been discussed.

2. Experimental

The preparation of MREPs is very similar to the preparation of mesoporous metal oxides invented by Yang et al[33]. For a typical preparation, 0.005mol of Rare earth(III) (La, Eu, Ho, Yb, Er) oxide was dissolved in 3.5g of concentrated HCl(36%), then the solution was heated to remove water and all other volatiles. The resulting solid was diluted in ethanol(60ml) and the template $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ (designated as P123, 0.84g) was added. Then the result mixture was stirred to be a clear solution and precipitated by the addition of 1.17g (0.01mol) of concentrated H_3PO_4(85%). Then the mixture was heated at 40°C overnight to evaporate ethanol slowly and then it was dried at 60°C for an additional 2hrs. Finally, the resulting solid was calcined in air from room temperature to 550°C with a heating rate of 1°C/min and kept at 550°C for 6hrs to remove the template. The final product obtained was mesoporous rare earth phosphate. For comparison, the rare earth phosphates (REPs) without the addition of template were prepared by precipitation method. The preparation method was as follows: 0.005mol of Rare earth(III) (La, Eu, Ho, Yb, Er) oxide was dissolved in 3.5g of concentrated HCl(36%). Then the solution was heated to remove water and all other volatiles. The resulting solid was diluted in water(60ml) and 1.17g(0.01mol) concentrated H_3PO_4(85%)was added. The resulting mixture was stirred to uniformity for 1h. Then $NH_3 \cdot H_2O$(10%)was added to adjust the pH at 4~5. The resulting mixture was aged overnight and was recovered by filtering off, washing, and dried at 110 °C for 12 h. Finally, the resulting solid was calcined at 550°C for 3 h. All samples were crushed and sieved to 20~40 mesh before be used in O-methylation reaction.

The powder X-ray diffraction (XRD) data were obtained by using an x-ray diffractometer (D/MAXIIB, Rigahu), operating at 40 kV and 10 mA, using Cu K radiation combined with Nickel filter. Transmission electron microscope (TEM) images were obtained using a JEOL JEM-2010 microscope operating at 200 kV.

The O-alkylation of hydroxybenzene was carried out in a fixed bed glass reactor with an internal diameter of 8mm. Before the reaction, the catalyst was pretreated at 350ºC for 3h in flowing dry N_2 stream. Then a mixture of hydroxybenzene and methanol(hydroxybenzene : methanol = 1:4(mol)) was fed to the reactor by a syringe pump at a space velocity(WHSV) of $1h^{-1}$ under N_2 flow(10ml/min). The reaction effluent were collected in an ice-trap and analyzed by GC equipped with a SE-60 capillary column. Before the data were obtained, reactions were maintained for a period of 1h at each temperature to ensure steady-state conditions.

3. Results and discussion

P123 is a poly(alkylene oxide) block copolymer structure non-ion surfactant, which possesses larger molecular configuration than most of other surfactants. It was utilized as a versatile template to synthesize mesoporous metal oxide and mixed metal oxides for the first time by Yang et al[33]. In this study, MREPs were also synthesized by using P123 as template. Fig. 1 shows the low-angle powder XRD patterns of MREPs calcined at 550°C. From Fig. 1, every trace of MREPs has a peak in 0.6~0.8° range, it indicates that mesoporous structure was preserved in the calcined MREPs. However, this structure was relatively disordered because the peaks were not clear except the (100) reflection. It can also

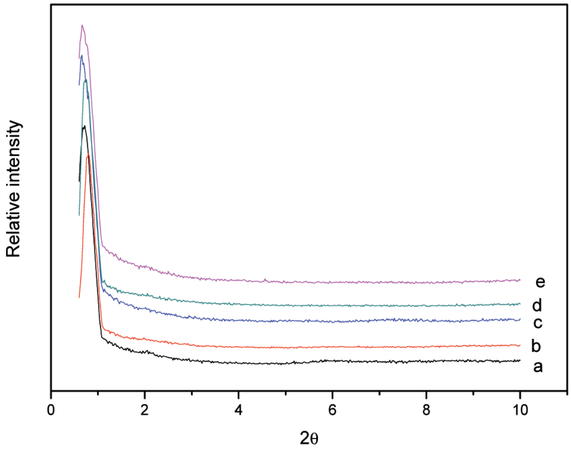

Fig. 1. Low angle powder XRD patterns of MREPs (a) $LaPO_4$ (b) $EuPO_4$ (c) $YbPO_4$ (d) $HoPO_4$ (e) $ErPO_4$.

be confirmed by the transmission electron microscopy(TEM) images obtained from sample of $EuPO_4$(Fig. 2).

Fig.2a, b show that $EuPO_4$ prepared with P123 has a mesoporous structure. In contrast $EuPO_4$ prepared without P123 has amorphous structure as shown in Fig. 2 c, d. It can be concluded that the template P123 played an important role for the mesoporous structure formation. At the same time, it can be seen from the TEM graphs that the shape of MREP was appeared to be disordered wormhole-like structure, which could be due to the effect of synthesis conditions and the raw materials. Anyway, the novel kind of MREPs materials were synthesized by the template method and the correlation fields of application were expected.

The application of this kind of MREPs in O-alkylation of hydroxybenzene was investigated. Table 1 summarized the catalytic performance of MREPs in the reaction of O-alkylation of phenol with methanol. From Table 1, MREPs show perfect selectivity for anisole at low reaction temperature, and the highest selectivity of anisole(100%) was obtained at 250~275°C. With the increasing of reaction temperature, the alkylation of ring and the selectivity of cresole increased. However the conversion of phenol increased with the increasing of reaction temperature till about 325°C, and then decreased with the continual increasing of reaction temperature. It could be attributed to the isomerization of anisole was enhanced at high reaction temperature.

The results of O-alkylation of catechol with methanol catalyzed by MREPs are presented in Table 2. From Table 2, MREPs also show perfect selectivity for guaiacol at low reaction temperature and the highest selectivity of guaiacol is nearly 100%. With the increasing of reaction temperature, O-alkylation of the other hydroxyl and alkylation of ring, the selectivity of veratrole and C-methylated products increased. But the conversion of catechol increased with the in-

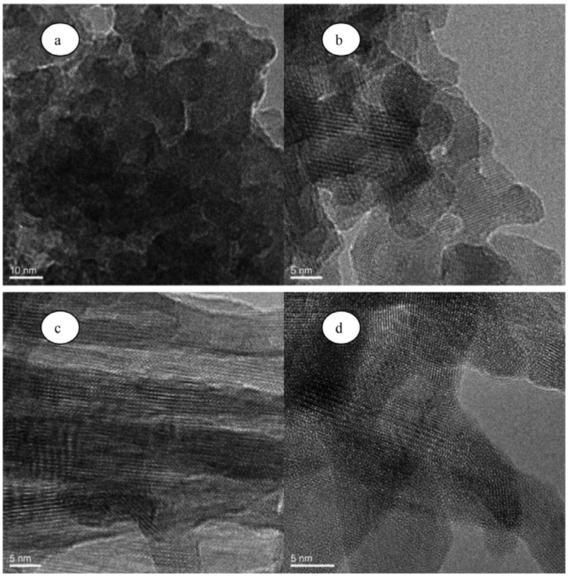

Fig. 2. TEM image of $EuPO_4$ (a) and (b) $EuPO_4$ prepared with P123 (c) and (d) $EuPO_4$ prepared without P123.

Table 1. Performance of O-alkylation of phenol with methanol Catalyzed by MREPs.

Catalyst	Reaction temperature(^oC)	Conversion (%)	Selectivity(%)		
			anisole	o-cresole	(m+p)-cresole
$EuPO_4$	250	9.4	100	0	0
	275	25	100	0	0
	300	58.7	92.5	7.5	0
	325	74.7	67	19.2	13.8
	350	74	22.4	18.7	35.8
$HoPO_4$	250	21.3	100	0	0
	275	39.7	97.1	2.9	0
	300	62.8	96.8	3.2	0
	325	73.3	89.3	10.7	0
	350	67.6	60	22.2	17.8

Reaction conditions: WHSV = 1 h^{-1}, phenol: methanol = 1:4 (mol), N_2 = 10mL · min^{-1}

creasing of reaction temperature till about 325°C, then decreased with the continual increasing of reaction temperature. This result is very similar to the result of O-alkylation of phenol with methanol.

Table 2. Performance of O-alkylation of catechol with methanol Catalyzed by MREPs.

Catalyst	Reaction temperature(°C)	Conversion (%)	Selectivity(%)		
			Guaiacol	Veratrole	C-methylated
$EuPO_4$	250	56.4	98.2	0.5	1.3
	275	89.1	92.3	4.4	3.3
	300	99.2	83.4	9.7	6.1
	325	100	66.7	12.5	12.4
	350	92.8	67.7	9.3	15
$LaPO_4$	250	65.4	99.1	0	0.7
	275	97.2	98.9	0.7	0.4
	300	100	98.2	1.5	0.3
	325	100	92.4	4	2.9
	350	87.9	81.3	6.3	6.7

Reaction conditions: WHSV = 1 h^{-1}, catechol: methanol = 1:4 (mol), N_2 = 10mL · min^{-1}

Many researchers have discussed the effect of active sites in O-alkylation of hydroxybenzene, however, the studies about the effect of the structure of catalyst is limited. In fact, the active sites of catalyst can be affected by the catalyst structure in the same catalyst composition. In the foregoing part, we have characterized the structure of mesoporous $EuPO_4$ and the corresponding REP by TEM measurement. For understanding the novel MREPs materials, the comparison of the performance of mesoporous catalysts with the catalysts prepared without templates has been studied (Fig.3 and Fig. 4). These two figures show that the yield of anisole and guaiacol are obviously higher for MREPs than those for the corresponding material prepared without P123 at low reaction temperature. Thus, the higher catalytic performance of mesoporous materials would be ascribed to their porous structure and much more amount of catalytic active sites. As we known, many reactions show low activity at low temperature. In order to obtain higher activity, higher reaction temperature is required. However, the higher reaction temperature will result in the production of more byproducts and formation of cokes, consequently accelerating the deactivation process of the catalysts. These MREPs presented higher conversion and selectivity at low temperature, as a result, they would be potential prior materials in catalysis.

4. Conclusion

Mesoporous rare earth phosphates have been synthesized by using P123 as template. The catalytic performance of this kind of MREP in O-methylation of hydroxybenzene has been studied. These MREPs exhibit higher catalytic performance in O-methylation of hydroxybenzene than the materials prepared without template at low temperature. The higher performance of these MREPs would be ascribed to their porous structure and much more amount of active sites. The

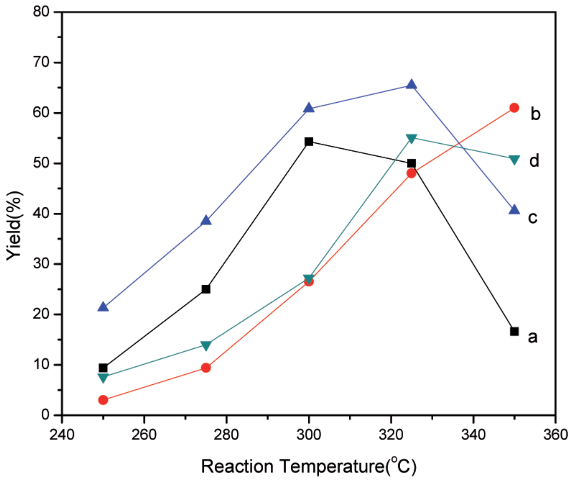

Fig. 3. Comparison of performance of MREPs with REPs in vapor O-methylation of phenol (a) $EuPO_4$ (mesoporous) (b) $EuPO_4$ (c) $HoPO_4$ (mesoporous) (d) $HoPO_4$.

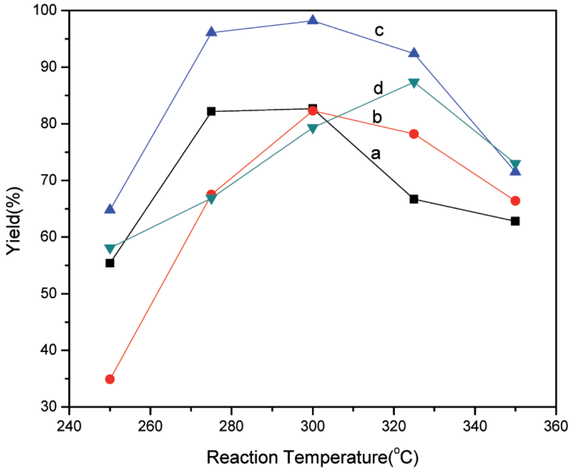

Fig. 4. Comparison of performance of MREPs with REPs in vapor O-methylation of catechol (a) $EuPO_4$ (mesoporous) (b) $EuPO_4$ (c) $LaPO_4$ (mesoporous) (d) $LaPO_4$.

characterization and applications of this kind of material are still under investigation.

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