Vapour phase *O*-alkylation of phenol over alkali promoted rare earth metal phosphates

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Abstract

The vapour phase synthesis of anisole by *O*-alkylation of phenol with methanol was investigated over lanthanum, cerium, samarium, and antimony phosphate catalysts promoted with cesium hydroxide. Among various catalysts investigated, the cesium promoted samarium phosphate provided better activity and selectivity. The effect of temperature, contact time, time-on-stream, reusability, and up-scaling of the catalyst were also studied. These studies clearly reveal that the Cs-Sm combination is the superior catalyst for selective *O*-alkylation of phenol with methanol. The unpromoted catalysts provided more *C*-alkylated side products. Incorporation of cesium suppressed the formation of side products. The X-ray diffraction analysis of various samples revealed that there is no change in the crystalline composition of the catalysts up on addition of cesium promoter. However, the surface acidity of the catalyst was observed to decrease after the incorporation of cesium promoter as revealed by the temperature programmed desorption study of anhydrous ammonia. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Alkylation is an interesting industrial organic reaction of most commercial utility. Products from every sector of the organic chemical industry are obtained making use of this methodology at some stage or other. Alkylation of phenol is an important reaction and alkylphenols are widely used in variety of applications such as antioxidants, herbicides, insecticides, polymers, and so on [1–3]. Alkylation processes normally require Friedel–Crafts acid catalysts such as AlCl$_3$, BF$_3$, TiCl$_4$, liquid HF, and AlCl$_3$ with elemental iodine. Several problems are associated with these catalysts such as toxicity, corrosiveness, low reaction selectivity, and disposal of effluents. In recent years, catalyst chemists turned their attention on the use of environment-friendly catalysts in place of mineral acids. Thus, several efforts are being made in the literature to replace the conventional homogeneous Friedel–Crafts catalysts by solid acids to fit in well with the concept of environmentally benign systems for eco-friendly processes. On these lines, several solid acid catalysts have been tried which include clays, heteropoly acids, sulphate-doped metal oxides, metal and mixed metal oxides, metal phosphates and zeolites [4–10].

The choice of catalyst system for alkylation is mostly based on the general acid–base characteristics (Brønsted, Lewis, strong or weak) of the materials. As per the literature reports, catalysts possessing strong acidic sites and strong basic sites favour ring

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alkylation while weak acid promoted base materials prefer *O*-alkylation [11]. Though a variety of catalytic systems have been employed for alkylation reactions, a direct correlation between reactivities of various catalysts with their acid–base properties is not well understood. Therefore, a systematic study was undertaken to gain knowledge on the possible relationship between the acid–base characteristics and the catalytic properties of some selected metal orthophosphate catalysts. The primary aim of this investigation was to devise a commercially viable catalyst system for vapour phase *O*-alkylation of phenol with methanol to anisole. Owing to the difficulties associated with the liquid phase alkylation processes such as long reaction time, high temperature, high pressure and secondary isomerization reactions, the vapour phase alkylation has been preferred. More details of the investigation are presented in this short communication.

2. Experimental methods

2.1. Catalyst preparation

An aqueous medium was used for the preparation of La, Ce, Sm and Sb metal phosphate catalysts investigated in this study. In a typical procedure, the required quantity of phosphoric acid (85% H_3PO_4) was taken in 1 l round bottom flask and refluxed at 90 °C for 1 h. The desired metal oxide was then added in portions over a period of 40 min under agitation. The temperature of the reaction was maintained at 90 °C for 3 h. The obtained product was filtered off, washed with distilled water, and dried at 110 °C for 12 h. Thus, obtained metal phosphate precursor was impregnated with 17 wt.% CsOH from cesium hydroxide (Aldrich, AR grade) aqueous solution by adopting a wet-impregnation method. The impregnated samples were oven dried at 110 °C for 12 h and calcined at 500 °C for 2 h in a closed electrical furnace in air atmosphere.

2.2. Catalyst characterization

The X-ray powder diffraction (XRD) patterns have been recorded on a Siemens D-5000 diffractometer by using Cu Kα radiation source and scintillation counter detector. The XRD phases present in the samples were identified with the help of ASTM powder data files. The FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer at ambient conditions, using KBr disks, with a nominal resolution of $4 \, cm^{-1}$ and averaging 100 spectra. A conventional all glass volumetric high vacuum (up to 1×10^{-6} Torr) system was used for BET surface area measurements. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature (−196 °C) by taking $0.162 \, nm^2$ as the area of cross-section of N_2 molecule. The temperature programmed desorption (TPD) measurements were made on AutoChem 2910 instrument (Micromeritics, USA). A thermal conductivity detector was used for continuous monitoring of desorbed ammonia and the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, the sample was pretreated at 200 °C for 1 h in a flow of ultra pure helium gas ($50 \, ml \, min^{-1}$). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He, $75 \, ml \, min^{-1}$) at 80 °C for 2 h and subsequently flushed with He ($60 \, ml \, min^{-1}$) at 100 °C for 2 h to remove the physisorbed ammonia. The hearing rate for the TPD measurements, from ambient to 1000 °C was $10 \, °C \, min^{-1}$. All flow rates mentioned are at normal temperature and pressure (NTP).

2.3. Activity studies

The *O*-alkylation of phenol with methanol was investigated in the vapour phase under normal atmospheric pressure, in a down flow fixed bed micro-reactor, at different temperatures. For each run, about 5–20 g of catalyst sample was packed between two plugs of quartz wool inside the glass reactor (Pyrex glass tube with i.d. 0.8 or 1.2 cm) and above the catalyst bed filled with glass chips in order to act as preheating zone. The reactor was placed vertically inside a tubular furnace which can be heated electrically.

The reactor temperature was monitored by a thermocouple with its tip located over the catalyst bed and connected to a temperature indicator-controller. A liquid mixture of phenol and methanol (1:9, v/v) were fed ($3–12 \, ml \, h^{-1}$) from a motorized syringe pump (Perfusor Secura FT, Germany) into the vaporizer where it was allowed to mix uniformly with nitrogen before entering the preheating zone of the

reactor. The N_2 gas from a pressure cylinder was used as the carrier and was maintained at a flow rate of 20–30 ml min^{-1} (NTP). The liquid products were collected at the bottom of the reactor in ice cold traps and were analysed by a gas chromatograph fitted with SE-30 Column and flame ionization detector (FID). The main reaction products observed were anisole and cresols with some unidentified products. The conversion, selectivity and yield was estimated as per the procedure described elsewhere [12].

3. Results and discussion

The activity and selectivity for O-alkylation of phenol with methanol was investigated between 300 and 400 °C. The activity and selectivity trends on various catalysts followed the same pattern with temperature. In general, an increase in the conversion with an increase in temperature was observed. The formation of some side products with traces of CO and CO_2 were also occasionally noted at higher temperatures. The change in conversion and selectivity as a function of contact time at a fixed temperature was also studied on various catalysts. For the purpose of better comparison, the activity and selectivity results obtained at an optimum temperature (350 °C) and contact time are shown in Table 1. The conversion and selectivity are calculated on phenol basis and almost all the excess methanol was recovered after the reaction. As can be noted from Table 1 that among various catalysts

investigated, the cesium promoted samarium phosphate shows maximum product yield (83%). Another important observation to be noted from Table 1 is that the cesium promoter decreases the C-alkylation products and enhances the O-alkylation product selectivity. Therefore, a thorough characterization study was undertaken on samarium phosphate catalysts to understand the precise role of Cs in increasing the product yield. After identification of suitable catalyst and optimization of reaction conditions like the temperature and life of the catalyst, further studies were carried out at different feed rates of the reactant and different flow rates of the carrier gas on cesium-doped samarium phosphate catalyst at a fixed temperature of 350 °C. It was observed that on increasing the liquid feed rate from 3 to 6 ml h^{-1} there was a decrease in the conversion and selectivity from 89 and 81% to 64 and 37%, respectively. Similarly, the conversion and selectivity was also found to be influenced by the flow rate of N_2 carrier gas due to the corresponding changes in the partial pressures of phenol and methanol and the contact times. At 22 ml min^{-1} of carrier gas flow rate, good conversion and product selectivity were observed. Replacement of N_2 gas with dry air resulted in the decrease of conversion and also formation of several side products. This is primarily due to a direct oxidation of both the reactants to various side products in the presence of oxygen present in the dry air.

The activity and selectivity of the Cs-Sm catalyst was found to be consistent with time-on-stream for several hours as shown in Table 2. Here, the

Table 1

Activity and selectivity of various unpromoted and promoted metal phosphate catalysts after 3 h of reaction at 350 °C and normal atmospheric pressure for O-alkylation of phenol with methanol. The catalyst amount 5.0 g, nitrogen flow rate 22 ml min^{-1}, and phenol and methanol mixture (1:9, v/v) flow rate 3.0 ml h^{-1}

Phosphate catalyst	Phenol conversion (%)	Selectivity (%)		Anisole yield (%)
		O-alkylation[a]	C-alkylation[b]	
La	82	83	14	68
Cs-La	85	84	12	71
Ce	76	84	13	64
Cs-Ce	79	87	11	69
Sm	80	85	12	68
Cs-Sm	89	93	3	83
Sb	70	75	22	52
Cs-Sb	80	82	15	66

[a] Anisole.

[b] Alkyl phenols.

catalyst amount was increased to 20 g level and the corresponding liquid feed rate to 12 ml h^{-1}. As can be noted from Table 2, the activity and selectivity of the catalyst was found to be steady with time-on-stream up to the 12 h reported. However, after a prolonged time (more than 20 h), a small decrease in the conversion and change in the product distribution was noted where

the C-alkylated product (p-cresol) increased at the expense of O-alkylated product, anisole. The original selectivity of the catalyst was regained after its re-generation at 350 °C for 4 h in a flow of dry air. In view of its better and consistent performance further studies were under taken to evaluate the same catalyst combination in a mini pilot plant at 2–5 kg catalyst
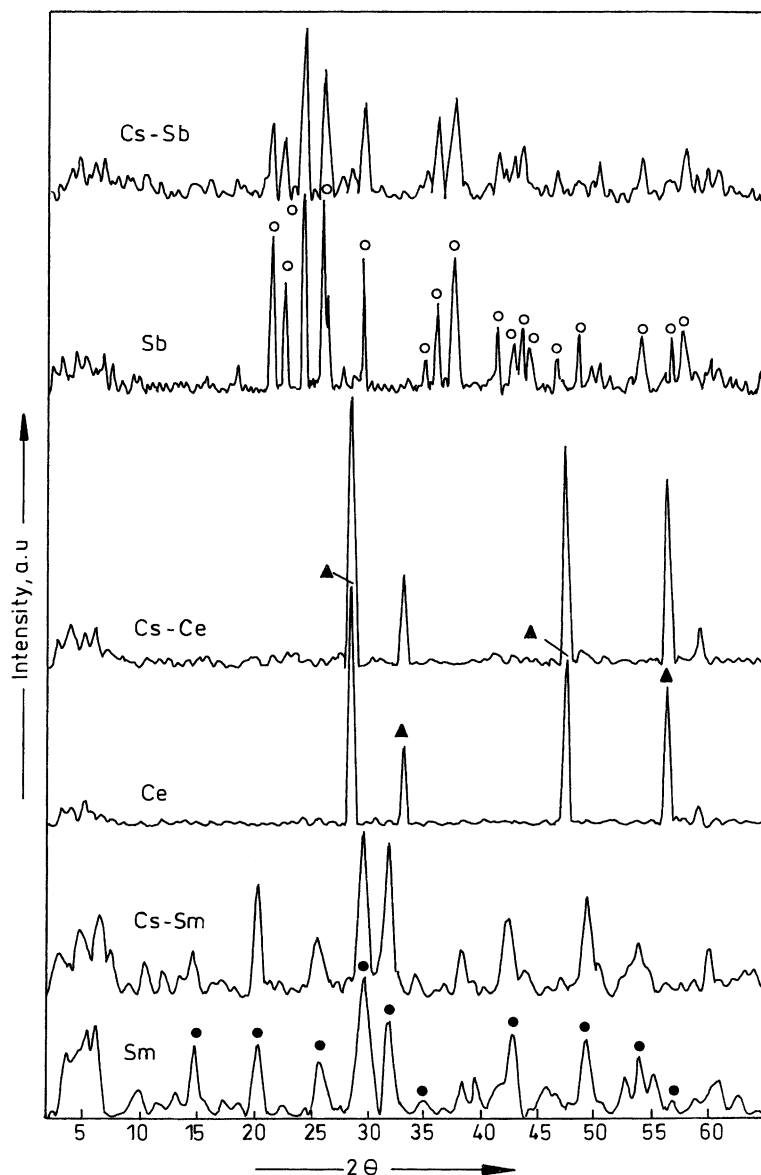

Fig. 1. XRD patterns of Sm, Cs-Sm, Ce, Cs-Ce, Sb and Cs-Sb phosphate catalysts: (●) lines due to samarium phosphate hydrate; (▲) lines due to cerium oxide; (○) lines due to antimony phosphate.

Table 2
Activity and selectivity of Cs-Sm catalyst with time-on-stream at 350 °C and normal atmospheric pressure for *O*-alkylation of phenol with methanol. Catalyst amount 20.0 g, nitrogen flow rate 30 ml min^{-1}, and phenol and methanol mixture (1:9, v/v) flow rate 12.0 ml h^{-1}

Time-on-stream (h)	Phenol conversion (%)	Selectivity for anisole (%)	Anisole yield (%)
1	86	89	77
2	83	91	76
3	86	96	83
4	84	92	77
5	86	90	78
6	83	91	76
7	85	90	76
8	84	92	77

level. Characterization studies and improvement in the physicochemical and mechanical properties of this catalyst system were also undertaken simultaneously.

The XRD patterns of the promoted and unpromoted Sm, Ce and Sb phosphate catalysts are shown in Fig. 1. The well defined lines due the presence of samarium phosphate hydrate (JCPDS File Nos.

27-582 and 27-583) can be noted in the case of samarium phosphate catalyst. Incorporation of cesium hydroxide to the samarium phosphate has no influence on the XRD patterns of this sample. In the case of cerium phosphate catalyst, the XRD lines due to cerium oxide (JCPDS File No. 4-593) were found to dominate. Apparently, the cerium oxide precursor has not been converted totally into the corresponding phosphate during the preparation stage. However, in the case of antimony system a clear formation of antimony phosphate (JCPDS File No. 23-793) is noted. Here again, no change in the XRD patterns of the SbPO$_4$ has been observed after incorporation of cesium hydroxide. Similar results were also noted in the case of lanthanum phosphate catalyst. Here too, the Cs promoter was observed to show no influence on the bulk crystalline composition of the La-phosphate catalyst. The XRD results thus indicate that the cesium promoter apparently changes the surface acid–base properties of the catalysts and has no influence on the bulk crystalline structure. The FTIR results also supported these observations. No change in the FTIR spectra of the metal phosphate catalyst was noted
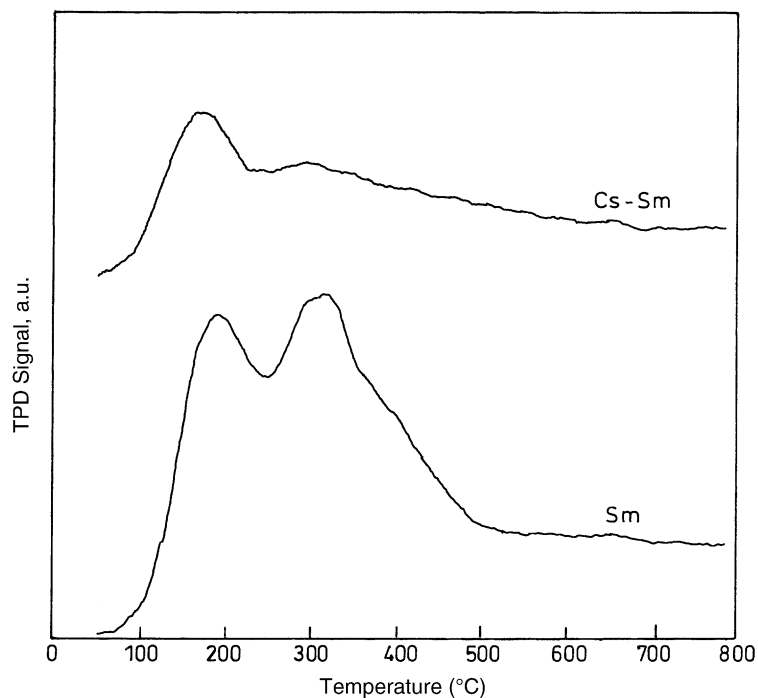

Fig. 2. The TPD of ammonia, after its adsorption over Sm and Cs-Sm phosphate catalysts at 80 °C and subsequent flushing at 100 °C.

Table 3

Temperature at peak maximum (T_m) and amount of ammonia desorbed from ammonia TPD on Sm and Cs-Sm phosphate catalysts. Sample weight about 0.2 g, He flow rate 50 ml min^{-1} and rate of heating 10 °C min^{-1}

	Sm		Cs-Sm	
T_m (°C)	185	317	163	308
ml NH$_3$ g^{-1} (STP)	5.596	8.596	1.440	0.077
Total ml NH$_3$ g^{-1} (STP)	14.192		1.517	

after incorporation with Cs promoter. The BET surface areas of all the investigated catalysts were found to be in the range 6–10 m^2 g^{-1}. Here too, the addition of Cs promoter had no major influence on the BET surface areas of these catalysts investigated.

The TPD of ammonia over the Sm and Cs-Sm phosphate catalysts is shown in Fig. 2 and the corresponding results of T_m and the amount of NH$_3$ desorbed are presented in Table 3. Presence of two TPD peaks for both the samples indicate that there are at least two types of different acid sites. The total amount of ammonia desorbed in the case of Sm was observed to be much higher than that of the Cs-Sm sample (Table 3). A substantial decrease in the quantity of NH$_3$ desorbed in the case of Cs-Sm catalyst indicates that the Cs promoter highly influences the surface acidity of Sm-phosphate catalyst. Further, the shapes of the TPD curves and the amount of NH$_3$ desorbed indicate that the Cs promoter has major influence on the strong acid sites of the catalyst. Further studies are highly essential to fully resolve the exact nature of the acid sites existing on the samarium phosphate catalyst. Nevertheless, the Cs-Sm combination catalyst exhibits better catalytic performance for the vapour phase *O*-alkylation of phenol with methanol to anisole.

4. Conclusions

The following conclusions can be drawn from this study: (1) Among La, Ce, Sm and Sb metal phosphate catalysts investigated, the samarium phosphate catalyst shows promising catalytic properties for the selective conversion of phenol and methanol to anisole. (2) The Cs promoter enhances the anisole product selectivity by suppressing the *C*-alkylated side products. (3) The Cs promoter was found to show no influence on the bulk structure of the catalysts. However, it decreases drastically the surface acidity of the phosphate catalysts. Further studies are, however, highly essential in order to understand the microscopic mechanism of this reaction and the inter-relationships between the acid–base characteristics and the catalytic properties.

Acknowledgements

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