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Direct hydroxylation of benzene to phenol by nitrous oxide on amorphous aluminium-iron binary phosphates

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ABSTRACT

The effect of iron content (Fe/Al molar ratio = 0.01–1 equivalent to the iron percentages from 0.5 to 20.5 wt%) and thermal treatment (450–650 °C) of aluminium-iron phosphates, prepared by an ammonia gelation method, on their catalytic performances in the one-step hydroxylation of benzene to phenol by N_2O, has been investigated. The solids have been characterized by ICP-MS, EDX, XRD, DRIFT, DR UV–V, XPS, and N_2 adsorption techniques. The results obtained showed the critical role of iron content in the catalytic behaviour of binary phosphates while thermal treatment hardly had effect. Phosphates with a lower amount of iron exhibited the best yield to phenol that was similar to those reported in the literature for Fe-MFI type catalysts. Thus, yield to phenol of 22% (0.7 g_{Phe}/g_{cat} h) at 350 °C has been achieved on the binary phosphate with Fe/Al = 0.02 (1 wt% of iron) calcined a 450 °C, in which highly dispersed iron species exist.

1. Introduction

An important number of industrial products, mainly in the polymer field, use phenol as an intermediate, i.e. the phenolic and the bis-phenol A derived resins. More than 90% of the world's phenol production is based on the cumene (isopropylbenzene) route that implies three steps: the alkylation of benzene with propylene to produce cumene; the oxidation of the cumene to cumene hydroperoxide by a free-radical mechanism and the cleavage of this hydroperoxide to phenol and acetone catalyzed by a mineral acid [1]. This route is not environmentally friendly and, furthermore, provides a high amount of acetone exceeding the industrial market demand. The direct hydroxylation of benzene is a good alternative even though this reaction is one of the most difficult in the field of organic synthesis for a number of reasons, one of which being the fact that phenol is much more reactive towards oxidation than benzene. The reaction has been extensively investigated in the liquid phase as well as in the gas phase using different oxidant agents and homogeneous and heterogeneous catalysts. Thus, in the liquid phase the best results have been obtained using hydrogen peroxide with both homogeneous and heterogeneous catalysts based on transition metals [2–5], but the reaction in presence of molecular oxygen with a reducing reagent such as ascorbic acid, has also been widely investigated [6,7]. From the environmental point of view, the reaction in the gas phase is more advantageous than in the liquid phase although when using O_2 low conversion values (<5%) and severe deactivation are observed, as indicated by copper supported on ZSM-5 zeolites [8,9]. With H_2/O_2 mixtures, the conversion values increased slightly and no deactivation of the catalyst was observed employing fluidized bed reactors [10]. However, the highest yields to phenol have been obtained using N_2O as an oxidant. This oxide affords N_2 as the co-product, which makes it environmentally acceptable, and a high value of available oxygen (36.4 wt%) only exceeded by that of H_2O_2 (47 wt%) [11]. Furthermore, its use as an oxidant enables it to be eliminated which is an added advantage considering N_2O is a strong greenhouse gas [12]. An overview on the application of N_2O in organic synthesis as an oxidant as well as the description of a new technology for the production of inexpensive N_2O based in the oxidation of ammonia on α-alumina supported manganese-bismuth oxide has been given recently by Parmon et al. [13]. Fe-containing MFI zeolites are the most promising catalysts for this reaction with high selectivity values to phenol (>95%), although with problems of deactivation and in fact, have been the subject of extended research [13–20]. Nowadays, it is generally accepted that Fe is necessary for the reaction and that the iron species in the extra-framework position are the active sites. However, the structure and nuclearity of those active iron sites remain unknown owing to the fact that the

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preparation and pretreatment methods of the catalysts strongly affect the iron distribution. Panov et al. have reported that the activity depends only on the number of α-sites, which are associated to the presence of dinuclear complexes of bivalent iron located in the micropore space of the zeolite matrix [13–15]. The bivalent iron is oxidized by N_2O into the trivalent state with the deposition of the so-called α-oxygen [21]. The importance of aluminium for a good catalytic performance has also been indicated [19,20]. Taking this into account, our research is concerned with the study of some systems based on aluminium-iron-phosphorus (AlFePO), prepared by an ammonia gelation method, as catalysts for the direct hydroxylation of benzene.

As far as we know, this is the first time that iron phosphates prepared using this economic simple method have been applied for this reaction. On the other hand, iron phosphates have been reported as catalysts in the hydrocarbon selective oxidation reactions, as methane to methanol using O_2 or N_2O [22]. Likewise, we have previously reported the good catalytic behaviour of aluminium and aluminium-vanadium phosphates respectively, in the oxidative dehydrogenation of ethylbenzene to styrene [23] and in the production of phthalic anhydride from o-xylene using O_2 [24].

Here we specifically report on the preparation and catalytic behaviour of AlFePO systems with several Al/Fe molar ratios and thermal treatments in the direct hydroxylation of benzene to phenol by N_2O. The solids were characterized by X-ray diffraction (XRD); diffuse reflectance Fourier-transform infrared (DRIFT) and ultraviolet–visible (DR-UV–vis) spectroscopy; X-ray photoelectron spectroscopy (XPS); scanning electron microscopy (SEM) and nitrogen adsorption techniques.

2. Experimental

2.1. Catalyst preparation

The AlFePO systems were prepared from appropriate amounts of $AlCl_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ aqueous solutions and H_3PO_4 (85 wt%) in order to obtain Al + Fe/P = 1 molar ratio, by precipitation with aqueous ammonia and stirring at 0 °C until pH = 6.7. The solid obtained was then washed with 2-propanol, dried at 120 °C for 24 h and calcined in air for 3 h. It was denoted by AlFePO(x)T where (x) indicates the Fe/Al theoretical molar ratio (x = 0.01; 0.02; 0.1; 1) and T the calcination temperature. The iron percentage in those systems was 0.5, 1, 4 and 20.5 wt%, respectively. As a reference, an iron (FePO) and aluminium (AlPO) phosphates were also obtained and calcined in the same way as has been described for AlFePO systems. Furthermore, aluminium phosphate calcined at 350 °C was employed as a support of iron in the preparation of one Fe/AlPO supported system by wet impregnation. For this, desired volume of a 0.1 molar solution of $Fe(NO_3)_3{\cdot}9H_2O$ in methanol were added to the support in order to obtain iron percentage of 0.1 wt%. After 3 h of stirring, the methanol was eliminated under vacuum and the resultant solid calcined in air at 450 °C for 3 h. This system will be denoted as 1Fe/AlPO-450. Before the calcinations, all the solids were powder screened to <0.149 mm, to avoid internal diffusion limitations in the reactions.

2.2. Catalyst characterization

The bulk composition of the solids was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis on a Perkin-Elmer ELAN DCR-e instrument. The samples were completely dissolved in HNO_3, 2 wt%, diluted to suitable concentrations and measured against standard solutions using PE Pure Plus atomic spectroscopy standards also from Perkin-Elmer. The final percentage is the average of three measurements being the estimated error of P (<2%), Al (<3%) and Fe (<4%).

The textural properties were determined from the adsorption–desorption isotherms of nitrogen at its liquid temperature, using a Micromeritics ASAP 2000 apparatus. Prior to measurements, all samples were degassed to 0.1 Pa.

XRD patterns were obtained using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Finely ground samples were scanned at a speed of 2°/min (2θ = 2–80°) using a Siemens D-500 diffractometer (40 kV, 30 mA).

SEM studies were carried out in a Jeol apparatus, model JSM 6300, equipped with an Oxford Instruments detector, model Link ISIS which allows the chemical analysis by energy dispersion of X-rays (EDX) of the studied solid surface. The measurements were repeated at least three times on different zones of the solid surface (experimental error ≤5%).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a FTIR instrument (Bomem MB-3000) equipped with an "environmental chamber" (Spectra Tech) placed in a diffuse reflectance attachment (Spectra Tech, Collector). A resolution of 8 cm^{-1} was used with 256 scans averaged to obtain a spectrum from 4000 to 400 cm^{-1}. DRIFT spectra were recorded after sample dilution to 15 wt% in KBr, and equilibrated for at least 1 h at 300 °C in a N_2 flow of 50 cm^3/min.

Diffuse reflectance spectra in the UV–vis region (200–800 nm) were collected at room temperature with a Variant Cary 1E UV–vis spectrophotometer equipped with reflectance attachment using $BaSO_4$ as reference.

XPS measurements were performed at room temperature in a hemispherical energy analyzer (MCD PHOIBOS-150, SPECS) with a conventional X-ray source (XR-50, SPECS, Mg-K_α, 1253.6 eV) working in a "stop-and-go" mode in order to reduce possible damage due to sample irradiation. Samples were kept at room temperature overnight under high vacuum (<10^{-6} Torr) before being transferred to the analysis chamber. Spectra were corrected for charging effects using the residual carbon peak C 1s at 284.8 eV. The binding energy values for identical samples were, in general, reproducible to within ±0.1 eV. The CasaXPS program was used for the deconvolution of the spectra.

2.3. Hydroxylation of benzene

Benzene hydroxylation was carried out in a previously described continuous-flow fixed-bed reactor at atmospheric pressure [24]. The reaction system has a valve which allows the feed composition or the effluent from the reactor to be analyzed at any time on stream. An analysis of reagent and product composition was carried out on-line using a multicolumn gas chromatograph equipped with FID and TCD detectors in parallel. N_2O and N_2 as well as O_2 and carbon oxides, if obtained, were separated in two columns in series, Porapak Q and Molecular Sieve 5A and analyzed by the TCD, whereas benzene and its corresponding reaction products were separated in a DB-1 capillary column and detected by FID. The quantitative analysis was carried out from the calibration standards. The catalyst was pre-treated at the reaction temperature for 1 h in a He flow (40 cm^3/min). Benzene was fed by means of a microfeeder. The standard experimental conditions: $F_{benzene} = 1.13 \times 10^{-4}$ mol/min; benzene/N_2O = 0.3 molar ratio; W = 0.2 g; F_{He} = 40 cm^3/min; T = 350 °C, were mainly taken after studying the influence of the temperature and B/N_2O molar ratio on the yield to phenol. Products were identified by gas chromatography–mass spectrometry. Benzene conversion (X) and selectivity to products (S_i) are expressed as mol% on a C atom basis. N_2O conversion was calculated from the amount of N_2 formed and of N_2O unreacted. Blank runs showed the reactor walls to be