

Partial oxidation of toluene by O₂ over mesoporous Cr–AlPO

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Abstract

The synthesis of mesoporous Cr–AlPO was carried out under hydrothermal conditions. Characterisation of the catalyst was done with low angle XRD, N₂ adsorption, UV–VISDRS, ESR and thermal analysis. The catalytic activity was tested for partial oxidation of toluene with molecular oxygen in vapour phase. It was observed that Cr–AlPO functions both as acid and redox catalyst. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The incorporation of transition metal ions into the framework sites of microporous aluminosilicates and aluminophosphates has been reported in the literature and resulting systems are potential catalysts for various selective redox reactions [1–3]. Oxidation of alkylbenzenes is one of the interesting reactions because of the importance of the products for various industrial applications. Both homogeneous and heterogeneous catalysts have been used for these reactions [4,5]. But for the large-scale production of fine chemicals, replacement of conventional homogeneous systems by heterogeneous catalysts will be advantageous in

the sense of catalyst recovery and reduction of undesirable side reactions. In liquid phase, these reactions have been catalysed by variety of heterogeneous microporous catalysts like TS-1, VS-1, CrS-1 with peroxides as oxidants [1,4,6]. Cr–AlPO-5 was shown to be an active and recyclable catalyst for the oxidation of alkylbenzenes with either TBHP or O₂ [7]. However, the activity of microporous catalyst is limited due to the pore size and stability of the active metal ion in the microenvironment. With the recent discovery of mesoporous materials, the activities of chromium containing MCM-41, MCM-48, HMS have been tested for the oxidation of alkylbenzenes with peroxides as oxidants [8–10]. However, the potential of chromium containing porous solid catalysts in liquid phase is limited because of the leaching of the active metal from framework. Moreover, it is always desirable to choose molecular oxygen as oxidant due to its availability in the nature. The potential of chromium containing

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catalysts can be increased by using molecular oxygen as oxidant and thereby carrying the reaction in vapour phase it is possible to control the leaching of chromium from the framework. In this communication, the synthesis, characterisation and catalytic activity of mesoporous Cr–AlPO for toluene oxidation with molecular oxygen are reported.

2. Experimental

2.1. Synthesis

Mesoporous chromiumaluminophosphates were prepared using cetyltrimethylammoniumbromide (CTAB) as surfactant and with the following gel composition. $\text{Al}_2\text{O}_3:x\text{P}_2\text{O}_5 : y\text{Cr}_2\text{O}_3:z\text{CTAB:TM AOH:wH}_2\text{O}$, where $x = 2.0\text{--}2.5$, $y = 0.01\text{--}0.2$, $z = 0.4\text{--}0.5$ and $w = 300\text{--}350$. Various sources of aluminium have been tried and aluminium hydroxide has been chosen as the source. Chromium nitrate was used as transition metal precursor. The pH of the gel was maintained at 9.5 with tetra methyl ammonium hydroxide, as the use of other sources like NaOH and NH_4OH resulted only in the amorphous materials. The resulting gel was aged at room temperature for 3 h, transferred into a stainless steel autoclave and hydrothermally treated at 423 K for 24 h. The solid was filtered, washed several times with deionised water and calcined at 773 K for 6 h to remove the organic template.

2.2. Experimental setup and procedure

The experimental setup consisted of three parts: the gas supply system, the reactor and the analysis system. The gasses O_2 (99.995%), and Ar (99.998%) (Carba-Gas, Lausanne, Switzerland) were used without further purification. The feed was regulated through mass flow controllers. Flow A contained oxygen, argon and toluene vapour. Flow B was used for the pretreatment of the catalyst with oxygen diluted in argon. Gas mixtures A and B were mixed at a pressure of 101 kPa. The loading of the catalyst and the gas flow were maintained constant throughout the study at 0.2 g and 1 ml/s. The catalyst was diluted with quartz

powder in a 1:1 ratio. All lines and valves were heated up to 423 K in order to avoid the condensation of the products. The catalyst was pretreated in O_2 (40-vol% O_2 , rest Ar) at 573 K before the reaction. The temperature was decreased and the flow was switched to the mixture of 2 vol% toluene plus 40-vol% O_2 in Ar.

2.3. Characterisation of the catalyst and reaction products

Various techniques have been used for the characterisation of the materials synthesised. The low angle X-ray diffraction pattern of the sample was recorded on a Siemens D 500 ($\theta/2\theta$) using monochromatised Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of $1^\circ/\text{min}$ over the range $2 < 2\theta < 10^\circ$. Thermal analyses of the samples were made with thermal analyser (Perkin-Elmer model TGA 7) at a heating rate of $20^\circ\text{C}/\text{min}$. Diffuse reflectance UV-VIS spectroscopy was carried out on a Cary 5E UV-VIS-NIR spectrophotometer. ESR spectra were recorded with Varian E-112 spectrometer at room temperature. N_2 adsorption-desorption measurements at 77 K were made using CE instruments, Sorptomatic 1990. The sample was out gassed at 473 K for 12 h. X-ray photoelectron spectroscopic measurements (XPS) for Cr_{2p} were performed on a PHI-550 ESCA-System (Perkin-Elmer GmbH). A Blazers QMG-421 mass-spectrometer and a Perkin-Elmer Autosystem XL gas chromatograph were used for the gas phase analysis. Toluene and organic products were separated in an SPB-5 capillary column and analysed by a FID. Ar/ O_2 , CO, CO_2 and H_2O were analysed in a Carboxen-1010 capillary column and analysed by a TCD.

3. Results and discussion

3.1. XRD

XRD patterns of as-synthesised and calcined AlPO, Cr–AlPO are shown in Fig. 1. XRD patterns of AlPO show low angle peaks typical for hexagonal phase. The as-synthesised Cr–AlPO material shows a maximum intense peak corre-

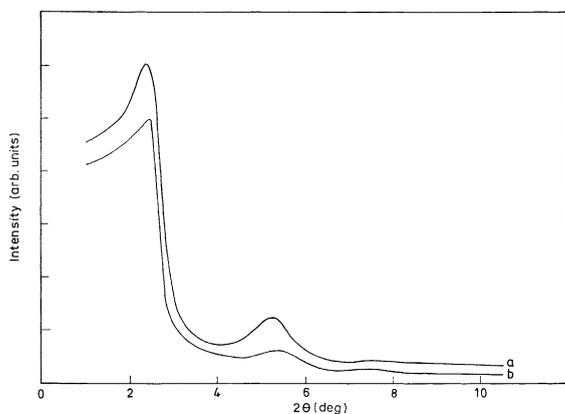


Fig. 1. XRD pattern of Cr–AlPO: (a) uncalcined, (b) calcined.

sponding to (100) reflection followed by weaker but clear peaks corresponding to (110) and (200) reflections that can be indexed on the basis of a hexagonal lattice. After calcination, broadening of the maximum intense (100) reflection with a slight decrease in *d* spacing value was observed. In the case of Cr–AlPO, intensity of the XRD peak is less compared to AlPO material. However, the sample retained its hexagonal structure after calcination.

An organic base, tetramethylammonium hydroxide (TMAOH), was used to maintain the pH of the gel. However, with NaOH and NH₄OH only amorphous materials were formed. The function of organic ammonium cation from TMAOH is probably to modify the strength of the electrostatic interactions between the aluminophosphate species and the cationic surfactant micelle assembly to form the S⁺I⁻/TMA⁺ ion pair. If either NaOH or NH₄OH is used, the smaller cations Na⁺, NH₄⁺ compete with the aluminophosphate species and thus restrict the interaction with the positively charged cationic surfactant. As stated earlier, aluminium hydroxide may form a less polymerised aluminophosphate with many hydroxyl groups and favour the assembly of the mesostructure compared to other aluminium sources [11,12].

3.2. Thermal analysis

Thermogram of as-synthesised ALPO shows mainly two weight loss regions one corresponding

to loss of physi-sorbed water below 373 K. The second and the main weight loss was observed in the temperature range 450–550 K corresponding to loss of organic template. It was observed that the AlPO is stable up to 1073 K.

3.3. N₂ adsorption

Nitrogen adsorption–desorption isotherms of the Cr–AlPO are shown in Fig. 2. For all samples, the isotherms are similar having inflection around $p/p_0 = 0.2–0.3$ characteristic of mesoporous materials. BET surface area and BJH pore size distribution for various catalysts are given in Table 1. It was observed that Cr–AlPO exhibit type IV isotherm with a hysteresis characteristic of mesoporous material. BET surface areas of the AlPO and Cr–AlPO are ~645 and ~500 m²/g, respectively. The decrease in the surface area of the Cr–AlPO compared to AlPO could be due to partial loss of crystallinity, which is in agreement with the observation from XRD. In both the cases the pore size is around 29 Å.

3.4. UV–VIS DRS

UV–VIS spectroscopy is a technique for the characterisation of transition–metal-incorporated zeolites [13–15]. Fig. 3 shows UV–VISDRS spectra of as-synthesised and calcined Cr–AlPO samples. As-synthesised material shows bands around 610, 440 and 270 nm. These bands are characteristic of

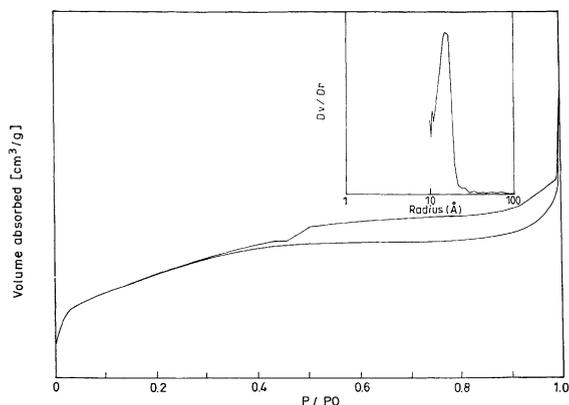


Fig. 2. N₂ adsorption–desorption isotherms of Cr–AlPO.

Table 1
Physico-chemical properties of AlPO materials

| Catalyst | d_{100} [uncal] (Å) | d_{100} [cal] (Å) | $a = 2$ $d_{100}/\sqrt{3}$ (Å) | BET surface area (m ² /g) | Pore size (Å) | Pore volume (cc/g) |
|----------|-----------------------|---------------------|-----------------------------------|--------------------------------------|---------------|--------------------|
| AlPO | 34.5 | 33.0 | 38.10 | 685 | 28 | 0.65 |
| Cr–AlPO | 35.0 | 33.4 | 38.56 | 490 | 29 | 0.51 |

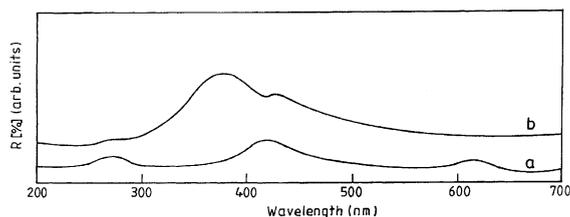


Fig. 3. UV–VISDRS of Cr–AlPO: (a) uncalcined, (b) calcined.

trivalent chromium in octahedral co-ordination. Due to the large difference in LFSE values of Cr(III) for tetrahedral (66.9 KJ/mol) and octahedral (224.5 KJ/mol) geometries, chromium atoms in as-synthesised material mainly occupy extra framework sites [16–18]. Upon calcination, a new charge transfer band at 370 nm along with a shoulder at 440 nm was observed. This CT band could be due to O (2p) \rightarrow Cr⁶⁺ (3d⁰) and/or Cr⁵⁺ (3d¹) charge transfer transitions viz., chromate or dichromate like species in tetrahedral environment [19].

3.5. ESR spectroscopy

ESR spectra of as-synthesised and calcined Cr–AlPO are shown in Fig. 4. As-synthesised material shows a broad singlet with a g value of 1.98 indicating Cr³⁺ ions in octahedral co-ordination [20,21]. ESR spectra of calcined Cr–AlPO shows g value at 1.95 characteristic of pentavalent chromium in tetrahedral or distorted tetrahedral co-ordination. ESR signal intensity decreased with increase in sharpness after calcination.

3.6. Catalytic activity

Table 2 gives typical results for the oxidation of toluene in the temperature range 523–648 K

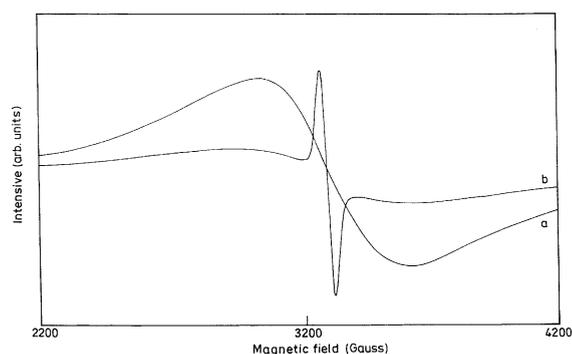
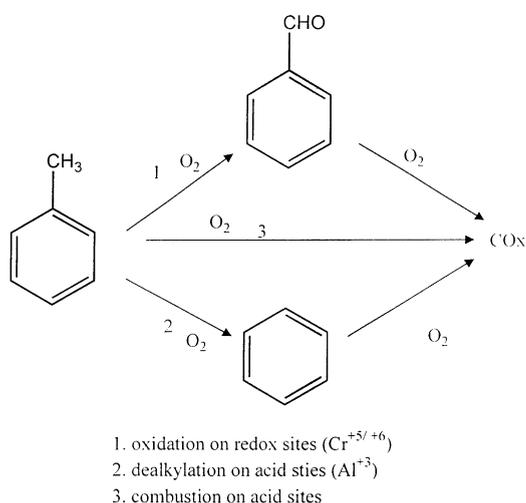


Fig. 4. ESR spectra of Cr–AlPO: (a) uncalcined, (b) calcined.

over Cr–AlPO catalyst. Benzaldehyde, benzene, CO₂ and CO are the reaction products. The reaction sequence is given in Scheme 1. The absence of coupled products indicates that radical mechanism is not taking place, rather surface type of reaction is possible where toluene adsorbs on the surface parallel to the lattice. It is clear that on the surface of the catalyst both oxidation and dealkylation reactions are taking place simultaneously leading to benzaldehyde and benzene. The formation of benzene, as a result of dealkylation reaction predominates on acid (Al³⁺) sites, whereas on redox sites (Cr^{5+/6+}) oxidation of toluene is taking place leading to benzaldehyde. At lower temperatures, redox properties of Cr–AlPO influence the reaction leading to the formation of benzaldehyde in excess and as the temperature is increased the selectivity towards benzene increases, indicating the dominance of acid sites. It was observed that with the increase of the temperature, the conversion of the toluene and selectivity of benzene increased. The catalyst was reused after calcination in air for 5 h at 673 K, which showed the same activity for the successive runs. Coke formation was not detected to any significant extent.

Table 2
Catalytic activity of Cr–AlPO for the oxidation of toluene with molecular oxygen

| Temperature (K) | Conversion of toluene (%) | Product selectivity (%) | | |
|-----------------|---------------------------|-------------------------|---------|------------------------|
| | | Benzaldehyde | Benzene | (CO ₂ + CO) |
| 523 | 0.75 | 91.0 | 2.4 | 6.6 |
| 548 | 0.90 | 83.5 | 2.6 | 13.9 |
| 573 | 1.40 | 60.4 | 3.0 | 36.6 |
| 598 | 2.23 | 50.6 | 6.1 | 43.3 |
| 623 | 4.85 | 42.4 | 8.2 | 49.4 |
| 648 | 9.19 | 25.3 | 12.4 | 62.3 |



Scheme 1. Proposed reaction scheme for the toluene oxidation catalyzed by Cr–AlPO.

4. Conclusions

Cr–AlPO materials have been prepared by hydrothermal synthesis and found to have hexagonal MCM-41 like morphology. These materials have high surface area $\sim 500 \text{ m}^2/\text{g}$ and pores are in mesoporous range $\sim 29 \text{ \AA}$. UV–VIS and ESR techniques have confirmed the presence of Cr^{5+/6+} in the framework. Cr–AlPO catalysts have been shown to be active for the vapour phase oxidation of toluene with molecular oxygen. It has been observed that in Cr–AlPO both acidity (due to Al³⁺) and redox properties (due to Cr^{5+/6+}) are competing leading to benzene and benzaldehyde, respectively.

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