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Synthetic kenyaite as catalyst support for hydrocarbon combustion

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Abstract

Synthetic kenyaite is prepared in the system K_2O–SiO_2–H_2O. It is modified with cobalt and platinum in order to obtain catalysts for complete oxidation of *n*-hexane and benzene. The prepared samples are characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), differential thermal analysis (DTA), temperature programmed reduction (TPR) and Fourier transformed infrared (FTIR) spectroscopy. Co is loaded on kenyaite using ammonia method and classical impregnation. Bimetallic Co–Pt possess higher catalytic activity than monometallic cobalt for the oxidation of benzene, while, for hexane oxidation, the monometallic cobalt catalysts exhibit higher or close activity to that of Co–Pt samples. The catalysts prepared by ammonia method have better performance due to finer dispersion of the metal particles on the surface of the support.

Keywords: Kenyaite; Cobalt; Platinum; Hydrocarbon oxidation

1. Introduction

In 1967 Eugster [1] reported the discovery of two rare hydrous alkali silicate minerals, magadiite $Na_2O\cdot14SiO_2\cdot10H_2O$ and kenyaite $Na_2O\cdot22SiO_2\cdot10H_2O$ from the lake beds of Lake Magadi in Kenya. Minerals of similar composition were subsequently established by Sheppard et al [2] – makatite $Na_2O\cdot4SiO_2\cdot5H_2O$ and Johan and Maglione [3] – kanemite $Na_2O\cdot4SiO_2\cdot7H_2O$. The first syntheses of suchlike silicates were carried out at about 373 K in the absence of templates or structure directing agents, over a period from 1 week to 2 years [4–6]. Later syntheses aiming at getting purer phases at higher reaction temperatures (453 K) and short duration were carried out using templates [7]. All these natural or synthetic materials normally exhibit rosette-like crystal aggregate morphology with single crystal dimensions making difficult complete structural determination by conventional single crystal XRD methods. However, the layered structure of these silicates is well established due to successful intercalation [4]. Nuclear magnetic resonance spectroscopic studies of synthetic hydrous sodium silicates resulted in the model representation of the silicate layers in magadiite and kenyaite [8]. In the course of the comprehensive investigations of these materials the influence of various physicochemical parameters on their topology and stability was established, as well as numerous properties that promote their applications as cation exchangers, adsorbents, catalysts, and suspending agents [4,9]. Magadiite was used for benzene sorption from water [10]. Metalloaluminophosphates were used for preparation of pillared kenyaites, varying the pore dimensions through manipulation of the reaction conditions and were tested in cracking of dodecane, *m*-xylene isomerization and benzene alkylation [11].

Due to its high thermal stability, layered structure and high specific surface area kenyaite is a potential catalyst support for deep oxidation of volatile organic compounds (VOC). VOC elimination through catalytic oxidation is an important process since catalytic incineration takes place at temperatures much lower than those required for thermal incineration.

Cobalt oxide is reported to be quite promising among the metal oxides used for preparation of supported catalysts for the removal of VOC and due to its high activity and stability platinum has widely been used in complete hydrocarbon oxidation, especially for aromatic hydrocarbons [12–14]. Even

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though cheaper, cobalt taken alone is not so active in reactions of complete VOC oxidation and the addition of Pt may enhance the catalytic activity.

We now report results on the synthesis of kenyaite in the system K_2O–SiO_2–H_2O, its modification with Co and Pt, characterization by X-ray diffraction, SEM, TG-DTA, TPR, FTIR spectroscopy. Two methods for cobalt loading are used in order to obtain catalysts of different particle size as well as to study the influence of the cobalt oxide dispersion in the reaction of complete benzene and *n*-hexane oxidation. Hexane has been chosen because it is a component of many products related to industry. In atmosphere it participates in a radical reaction with $OH^{\bullet}$, yielding 2-hexanone, 2- and 3-hexyl nitrate and 5-hydroxy-2-pentanone, all of them existing in the photochemical smog. Benzene was chosen because it is a high toxic pollutant, difficult for oxidation.

2. Experimental

2.1. Sample preparation

Synthetic kenyaite was prepared following the procedure described by Feng and Balkus [7]. In a typical run 1.13 g of KOH (Merck) were dissolved into 100 g of distilled water, followed by 5.53 g highly dispersed of SiO_2 (Merck) and polyethylene glycol 200 (MW 259, Aldrich). The solution was brought to the boiling point and then stirred at room temperature for 40 min by a mechanical mixer at 200 rpm. The resulting homogenous gel of molar composition $1.2K_2O$–$10SiO_2$–$200H_2O$, had a pH value of 11. Next, it was transferred into a Teflon-lined autoclave. The crystallization was performed under static conditions at 453 K for a period of 96 h. The cooled run-product was washed with distilled water and dried at 373 K.

The proton form of kenyaite (Ken) was obtained by treatment of kenyaite with 1 M solution of ammonium nitrate at 353 K for 24 h and subsequent filtration, washing and calcination at 773 K. Cobalt was supported on the proton form of kenyaite by two methods. Classical impregnation with aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ was used to prepare the precursor which was subsequently dried and calcined for 1 h at 773 K in air (designated from here on as samples I). The second method applied was described by Barbier et al. as ammonia method [15]. It results in the formation of finely dispersed cobalt oxide on the support. In a typical procedure $Co(NO_3)_2\cdot 6H_2O$ was dissolved in water at room temperature. To prevent oxidation of Co^{2+} by dissolved oxygen the water was boiled and the system was protected from air by a nitrogen blanket. Ammonia was added into the solution resulting in precipitation of $Co(OH)_2$. After that the support was added to the solution and stirred for 2 h. Finally, the system was filtered, washed with water, dried under vacuum at 353 K and calcined for 1 h at 773 K in air (designated from here on as samples AM).

Platinum was introduced by impregnation with aqueous solution of $Pt(NH_3)_4Cl_2$ of the freshly prepared (not calcined) by ammonia method Co-containing samples, as well as, of those prepared by cobalt impregnation after their calcination. Platinum-loaded samples were dried overnight at 373 K and calcined additionally for 1 h at 773 K in air.

Monometallic platinum samples were prepared by impregnation in order to compare their catalytic activity with that one of the other samples.

2.2. Sample characterization

The powder XRD patterns were collected at room temperature in a step-scan regime (step = 0.02°, count time = 2 s) on a DRON 3 M diffractometer using Fe-filtered Co Kα radiation (λ = 1.7903 Å). The XRD data were processed using the program FIT [16]. The micrographs were taken with a Philips 515 scanning electron microscope (SEM). IR spectra were collected on a FTIR Bruker Tensor 37 spectrophotometer with a spectral resolution of $2\,cm^{-1}$, using a KBr pellet technique. TG-DTA was performed on a Stanton Redcroft thermal analyzer STA 780 with a heating rate 10 K/min under argon atmosphere. Specific surface area measurements for the calcined samples were carried out on a Micromeritics instrument FlowSorb 2300, using single point surface analysis. The amount of Co and Pt in the catalysts was determined by Varian ICP AES. Temperature programmed reduction (TPR) was carried out by equipment described elsewhere [17] using a flow mixture of 10% H_2 in Ar at 10 ml/min, temperature rate of 10 K/min to 973 K. Prior to the TPR experiment the samples were treated in Ar for 1 h at 423 K.

2.3. Catalytic tests

The samples were tested in the reaction of benzene and *n*-hexane complete oxidation. The tests were carried out in a flow type glass reactor at atmospheric pressure. The catalyst loading was 100 mg (fraction 0.8–0.63 mm). The catalyst temperature measurements were performed by a thin thermocouple positioned in the catalyst bed. Inlet benzene and *n*-hexane concentrations of 1400 and 2400 ppmv, respectively, at a total flow rate of 250 ml/min were used. External mass transfer limitations were minimized by working at high gas hourly space velocity (GHSV – $37{,}500\,h^{-1}$). Internal diffusion resistance was eliminated crushing of the catalyst pellets to size of 0.6–0.8 mm. The reactor used has an inner diameter of 8 mm, i.e. the ratio $D_r/D_p = 11$. The reaction products were analyzed by a Varian 3700 gas chromatograph equipped with thermal conductivity detector ($T = 333$ K, $T_{filament} = 353$ K), flame ionization detector ($T = 453$ K), and 2 m column with Porapak Q (0.150–0.180 mm, Riedel-de Haën AG D-3016 Seelze 1) operating at 443 K. Nitrogen was used as a carrier gas (30 ml/min). All gas lines of the apparatus were heated at 353 K in order to minimize the VOC adsorption on the tube walls. Mass flow controllers Matheson were used for stable control of gas flow rates. Benzene (Merck) and *n*-hexane (Fluka) were used both for oxidation and calibration. The gas chromatograph was calibrated against known concentrations of benzene and hexane. The conversion was calculated as the quantity of benzene (or hexane) converted over that one of the introduced reagent.