



Active phase, catalytic activity, and induction period of Fe/zeolite material in nonoxidative aromatization of methane



Pinglian Tan

Laboratory of Heterogeneous Catalysis, Anhui University of Technology, Hudong Road 59, Maanshan City, Anhui Province 243002, People's Republic of China

ARTICLE INFO

Article history:

Received 16 November 2015

Revised 28 January 2016

Accepted 30 January 2016

Available online 4 March 2016

Keywords:

Methane aromatization

Iron carbide

Fe/HZSM-5

Fe/HMCM-22

Pretreatment

XPS and XRD characterizations

Iron–carbene

ABSTRACT

Catalytic dehydroaromatization of methane has been investigated over 2–6 wt.% Fe-modified HZSM-5 or HMCM-22 zeolite in the absence of an added oxidant. After pretreatment in a CH₄/Ar/He mixture, Fe/HMCM-22, and more significantly, Fe/HZSM-5 exhibited high catalytic activity in nonoxidative conversion of methane to aromatic hydrocarbons. This conversion actually takes part in three consecutive steps, oxidation of methane by iron oxides, decomposition, and aromatization of methane. During this conversion, XPS and XRD results showed the gradual reduction of Fe₂O₃ to metallic Fe, followed by the carburization of the metallic species. The fact that no aromatic products were detected until iron carbide was formed demonstrated that carburized Fe was the active species for the aromatization of methane. Under the same reaction conditions, both metallic Fe and carburized Fe were highly effective for activation of methane, but they catalyzed dehydrogenation of methane to carbonaceous materials and to aromatics, respectively. Difference in the catalytic properties of those two Fe species suggested that carburized Fe could stabilize carbene, the primary intermediate of activated methane, possibly via formation of a metal–carbene complex, C–Fe=CH₂, so that carbene was able to dimerize into ethylene, which was then oligomerized to aromatics on the acid sites of the zeolite.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Nonoxidative aromatization of methane, a very abundant fossil fuel resource, is a novel and promising process that simultaneously produces high-value aromatic hydrocarbons and CO_x-free hydrogen [1]. This transformation has been performed with metal-based, especially transition-metal-based materials [2–5]. Unfortunately, up to now, only a small number of transition metals, such as Mo, Re, and Fe, have been found to be highly active for the aromatization of methane. Among those active metals, iron is the most abundant, stable, and environmentally friendly, showing great potential for industrial application. The promotional effect of Fe additive on the activity and stability of Mo/HZSM-5 in methane aromatization has been extensively studied [6–10]. On the other hand, single iron sites embedded in a silica matrix exhibited excellent performance in the conversion of methane to aromatics and ethylene above 1000 °C [5]. When the support silica was replaced with a suitable zeolite, aromatic products were detected at much

lower reaction temperatures and the catalyst preparation method became simpler. Weckhuysen et al. [11] first reported that after activation in O₂ or CO at 500 °C and then heating in He to the reaction temperature, 2 wt.% Fe₂O₃/HZSM-5 catalyst, prepared by the impregnation method, gave a methane conversion of ca. 4.2% and a maximum benzene selectivity of around 70% at 750 °C and space velocity of 800 ml g⁻¹ h⁻¹. Based on the results of X-ray photoelectron spectroscopy, they suggested that iron suboxides located on the external surface of the zeolite, formed via the reduction of Fe₂O₃ by methane, were the active phases for methane activation [12]. However, the reported active phase and induction period of Fe/HZSM-5 in methane aromatization are in contradiction to those of Fe/SiO₂ or Fe/Al₂O₃ in methane decomposition [13,14]. Another class of catalyst support that has been examined for this reaction is the HMCM-22 zeolite, but research work on methane aromatization over Fe/HMCM-22 has never been conducted.

In this work, catalytic dehydrogenation and aromatization of methane over 2–6 wt.% Fe/HZSM-5 and Fe/HMCM-22 materials in the absence of an added oxidant was investigated. XPS and XRD techniques were used for the identification of the phases present on the Fe-based catalyst during methane activation.

E-mail address: tanpinglian@sina.com

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite (Si/Al = 25) was supplied by Nankai University (Tianjin, People's Republic of China). HMCM-22 zeolite (Si/Al = 15) was synthesized according to the procedures described by Shu et al. [15] and Corma and Corell [16]. Fe/zeolite catalysts were all prepared via the impregnation method. Each 3 g portion of HZSM-5 or HMCM-22 zeolite was impregnated for 24 h at room temperature with 50 ml of aqueous solution of iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich) containing the required amount of iron. The resulting material was dried at 120 °C and then calcined in a Nabertherm furnace at 500 °C in air for 5 h. Finally, the freshly prepared Fe/zeolite samples were pressed, crushed, and sieved to 20–40 mesh for catalytic evaluation.

2.2. Catalyst evaluation

Catalytic tests were carried out in a continuous fixed-bed flow quartz reactor (7 mm ID) system at 750 °C and at atmospheric pressure. All gases used in this work were UHP grade without further purification. Typically, 0.4 g catalyst was heated in the reactor to 750 °C at a ramp rate of 22.3 °C min^{-1} . To remove adsorbed water and prereduce the catalyst, a gas mixture of 52 vol.% He, 43.2 vol.% CH_4 , and 4.8 vol.% Ar was introduced into the reactor at 25 ml min^{-1} during temperature-programmed pretreatment. Once catalyst temperature reached 750 °C, another gas mixture of 90 vol.% CH_4 and 10 vol.% Ar (10 ml min^{-1}) was introduced into the reactor in place of the pretreatment gas mixture through a mass flow controller (Brooks 5850E) and the catalyst test was started. Argon in CH_4 was used as an internal standard. All reactants and products were analyzed with two online gas chromatographs (Agilent 5820) equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. The reactor outlet pipeline and the gas sampling valves were kept above 160 °C to prevent product condensation that might cause plugging. CH_4 , C_2H_4 , C_2H_6 , C_6H_6 , C_7H_8 , and C_{10}H_8 were separated by a Porapak-P packed column and analyzed using the FID. H_2 , Ar, CO, CH_4 , and CO_2 were separated by an activated carbon packed column and analyzed using the TCD. All reaction rates were calculated based on carbon balance and were expressed as $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$. Methane conversion was calculated on a carbon number basis. The spent samples were cooled to room temperature quickly after reaction and kept under helium for their XPS and XRD measurements.

2.3. Catalyst characterization

Nitrogen adsorption at -196 °C was carried out on a Micromeritics automatic surface area and pore analyzer (TriStar II 3020). All of the samples were outgassed under vacuum at 350 °C for 5 h prior to analysis. The specific surface area was evaluated using the BET method, while the micropore surface area and micropore volume were determined according to the *t*-plot method.

Temperature-programmed desorption of ammonia (NH_3 TPD) was performed to determine the effect of the iron loading on the acidic properties of the resultant catalyst. A 0.1 g sample was first heated at 550 °C for 40 min, then cooled to 50 °C in helium, and then exposed to a gas mixture of 8 vol.% ammonia in helium for 40 min at the same temperature. After adsorption, the sample was purged with helium at 100 °C for 1.0 h to remove physically adsorbed NH_3 and then heated at a rate of 10 °C min^{-1} from 100 to 650 °C. A thermal conductivity detector was employed to monitor the amount of ammonia in the reactor effluent.

The Fe content was determined by ICP-AES (Optima 7300DV). The solutions for analysis were prepared by digesting 0.05 g of the dried sample (120 °C for 6 h) in a HF/HNO_3 (7:3, 10 ml) solution, followed by adding 2 ml HCl solution and then some deionized water up to 50 ml.

X-ray powder diffraction (XRD) patterns of HZSM-5 and Fe-modified HZSM-5 zeolites were obtained on an ARL X'TRA diffractometer using $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. Powder diffractograms were recorded over a 2θ range of 5–70° at a scanning speed of 5° min^{-1} .

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250 spectrometer equipped with a monochromatic Al $\text{K}\alpha$ X-ray source (1486.6 eV) operated at 15 kV and 150 W and a hemispherical energy analyzer. The base pressure in the analysis chamber was 1×10^{-9} Torr. Measurements were carried out at a detector takeoff angle of 90°. The spectra were recorded with pass energy of 30 eV, X-ray spot size of 500 μm , and step size of 0.05 or 0.1 eV. The $\text{Si}2p$ line at 103.4 eV was taken as a reference for binding energy (BE) calibration.

Near-surface atomic concentrations of the fresh and spent Fe/zeolite materials were calculated according to peak areas and sensitivity factors. Curve fitting of the XPS spectra was carried out using CasaXPS data processing software. Nonlinear Shirley background functions were used as provided by CasaXPS to modify the spectra for peak fitting. Curve-fitting procedures used for high-resolution spectra of Fe2p and C1s used 60:40 [17] and 80:20 Gaussian:Lorentzian (G:L) line shapes, respectively. Other deconvolution parameters including peak position and full width at half maximum (FWHM) of the Fe2p and C1s peaks are listed in Table S1 in the Supporting Information.

3. Results and discussion

3.1. Methane dehydroaromatization over Fe/HZSM-5 and Fe/HMCM-22 catalysts

Fig. 1A and Table 1 show the effect of Fe loading (2–6 wt.%) on the catalytic performance of Fe/HZSM-5 catalyst in methane dehydroaromatization at 750 °C and space velocity 1500 $\text{ml g}^{-1} \text{ h}^{-1}$. Benzene was always the major aromatic product in this investigation, accompanied by other heavier aromatic compounds including mainly naphthalene and a small amount of toluene. One can observe an initial aromatics formation rate ($r_{\text{Aromatics}}$) of 63.7 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ over 2 wt.% Fe/HZSM-5 catalyst. The $r_{\text{Aromatics}}$ increased with the time of reaction and reached a maximum value of 156.9 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ at a methane disappearance rate (r_{CH_4}) of 1847 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ at 1.5 h, but then declined slowly with increasing time on stream. After 4 h of reaction, an $r_{\text{Aromatics}}$ of 86.3 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ could still be obtained. The catalytic activity observed in this work is much higher than that reported in the literature [11]. Since both 2 wt.% Fe catalysts were prepared by the same impregnation method, the author deduces that during this catalyst pretreatment, both rapid removal of adsorbed water and prereduction with CH_4 played crucial roles in improving the catalytic activity of the material. Similar prereduction with CH_4/He (80 vol.% CH_4) prior to the reaction was found to markedly enhance the catalytic activity and aromatics selectivity of a 4 wt.% Mo/HZSM-5 sample in methane aromatization [18]. Tempelman et al. attributed this improvement of catalytic performance to the decrease in mobility of the metal species after prereduction with CH_4 [18]. With an increase in Fe loading, the catalytic activity of Fe/HZSM-5 gradually increased. A maximum $r_{\text{Aromatics}}$ of 190.2 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ at an r_{CH_4} of 2217 $\text{nmol}/(\text{g}_{\text{cat.}} \text{ s})$ was achieved on the 6 wt.% Fe catalyst.

Download English Version:

<https://daneshyari.com/en/article/60614>

Download Persian Version:

<https://daneshyari.com/article/60614>

[Daneshyari.com](https://daneshyari.com)