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ScienceDirect
Chinese Chemical Letters 22 (2011) 639–642
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Synergistic catalysis of isolated Fe^{3+} and Fe_2O_3 on FeO_x/HZSM-5 catalysts for Friedel–Crafts benzylation of benzene

Tao Lin, Xin Zhang *, Rong Li, Ting Bai, Si Ying Yang

School of Chemical Engineering, Northwest University, Xi'an 710069, China

Received 2 September 2010

Abstract

FeO_x/HZSM-5 catalyst with 8 wt.% Fe-loading (8-FeZ) exhibited significantly higher reactivity in the benzylation of benzene with benzyl chloride than FeO_x/HZSM-5 catalyst with 2.5 wt.% Fe-loading (2.5-FeZ) because the synergistic catalysis between isolated Fe^{3+} and superfine Fe_2O_3 occurred on 8-FeZ in the reaction.

Keywords: Friedel–Crafts; Synergistic catalysis; Benzene; Diphenylmethane; Fe^{3+}; FeO_x/HZSM-5

Friedel–Crafts benzylation of benzene with benzyl chloride (BC) is important for the production of high value diphenylmethane (DPM) which is used as pharmaceutical intermediates and fine chemicals [1]. Conventionally, homogeneous acid catalysts such as $AlCl_3$, BF_3 and H_2SO_4 are applied for the reaction [1,2]. However, these catalysts bring about some disadvantages, such as corrosion, toxicity, difficult separation and recovery. Therefore, it is highly desirable to develop heterogeneous solid catalysts to replace homogeneous catalysts.

Fe-based solid catalysts, such as Fe-HZSM-5 [3], Fe-SBA-15 [4] and Fe-MCM-41 [5] catalysts have been considered to be promising catalysts for the benzylation of benzene with BC [2]. Nevertheless, there are some debates on the active sites for the reaction. Choudhary et al. [3] thought that the reducible Fe species were relative to the reactivity of Fe-HZSM-5. Sun et al. [4] reported that the highly dispersed iron oxide nanoclusters on Fe-SBA-15 were active sites for the reaction. Arafat and Alhamed [5] considered that the high redox potential Fe^{3+} incorporated in the MCM-41 silica matrix and Fe_2O_3 were responsible for the high reactivity of Fe-MCM-41. Without deep understanding structure–reactivity relation, it is difficult to develop an efficient catalyst for the reaction.

Here, based on the results of kinetic studies and the properties of these catalysts characterized by X-ray diffraction (XRD) and UV–vis spectroscopy, we discuss roles of Fe species on the reactivity of FeO_x/HZSM-5 catalysts in Friedel–Crafts benzylation of benzene and substituted benzene (toluene, *p*-xylene) with BC.

In this work, FeO_x/HZSM-5 catalysts were prepared by incipient wetness method. Under stirring, powder HZSM-5 (SiO_2/Al_2O_3 = 25, Nan Kai Unv.) was impregnated by the calculated amount of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, Tianjin Oumi Chem., A.R.) aqueous solution to give 2.5 and 8 wt.% Fe-loading. The resultant mixture was dried at 110 °C for

* Corresponding author.
E-mail address: zhangxinzhangcn@yahoo.com.cn (X. Zhang).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2010.12.034

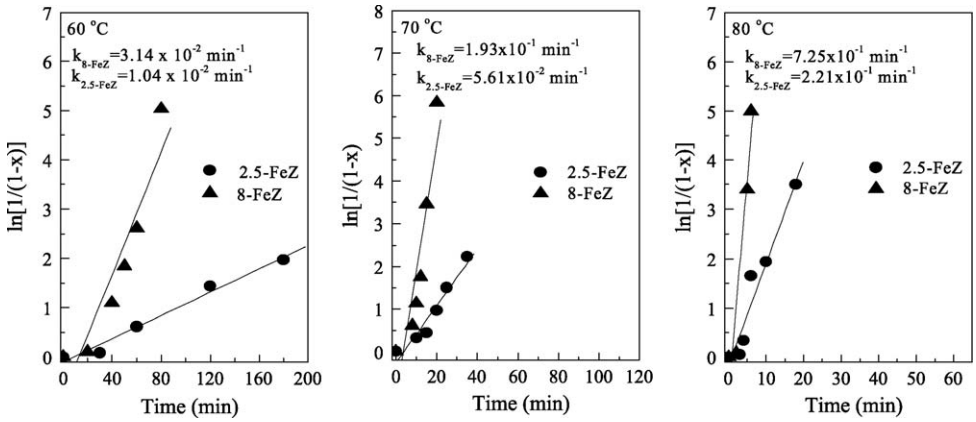

Fig. 1. Pseudo 1st order plots of benzylation of benzene with benzyl chloride on 2.5-FeZ and 8-FeZ catalysts at different temperature.

4 h and then calcined at 500 °C for 5 h in air. FeO_x/HZSM-5 catalysts with 2.5 wt.% and 8 wt.% Fe-loading are remarked as 2.5-FeZ and 8-FeZ, respectively.

Liquid phase benzylation of benzene and substituted benzene (toluene, *p*-xylene) with BC on these catalysts was carried out in a three necked round-bottomed flask (250 mL) equipped with a reflux condenser and magnetic stirring. The flask was heated in a precisely controlled water bath under atmospheric pressure. In a typical run, 30 mL benzene (toluene, or *p*-xylene) was added to 0.2 g catalyst placed in the flask and the mixture was heated to required reaction temperature. The mixture was maintained for 5 min at the temperature and then 2.7 mL BC was added. The moment was regarded as initial reaction time. The catalyst was separated from liquid mixture by centrifuge. Reactants and products were analyzed by gas chromatography (Schimadu GC-14C) with FID and packed column polyethene glycol (3 m). Since benzene was in excess, conversion was calculated based on BC.

Fe_2O_3 and HZSM-5 showed no activity in the benzylation of benzene with BC. It can be seen in Fig. 1, distinctive conversion of benzyl chloride with 100% selectivity of DPM (not shown in Fig. 1) was obtained on 8-FeZ and 2.5-FeZ under the investigated reaction conditions. Hence, the interaction of Fe with HZSM-5 occurred in these catalysts. In order to further evaluate the catalytic reactivity of 8-FeZ and 2.5-FeZ, kinetics of the benzylation of benzene with benzyl chloride on these catalysts were studied. It is hypothesized that the reaction rate of BC follows a pseudo-first-order rate equation, $\ln[1/(1-x)] = k(t-t_0)$, where k is the first-order rate constant (min^{-1}), x is the conversion of BC (mol%), t is the reaction time (min) and t_0 is the induction period (min). In addition, activation energy (E_a, kJ/mol) of the benzylation of benzene with BC on these catalysts is estimated from Arrhenius equation, $k = A\exp(-E_a/RT)$, in which A is the frequency factor (min^{-1}), R is the universal gas constant (8.314 J/(mol K)) and T is the reaction temperature (K).

The linear plots of $\ln[1/(1-x)]$ versus t was obtained by linear regression method and the rate constant k was calculated by these plots (Fig. 1). It is found that the reaction rate of BC could be fitted well to the *pseudo*-first-order rate law. Rate constant $k_{8\text{-FeZ}}$ (on 8-FeZ) and $k_{2.5\text{-FeZ}}$ (on 2.5-FeZ) gradually increased with the increase of reaction temperature. Hence, the rise of reaction temperature favored the conversion of BC on 8-FeZ and 2.5-FeZ. $k_{8\text{-FeZ}}$ is much higher than $k_{2.5\text{-FeZ}}$ under the same reaction conditions. Fig. 2 shows Arrhenius plots of the reaction on 8-FeZ and 2.5-FeZ catalysts. E_a on 8-FeZ is *ca.* 132.6 kJ/mol and E_a on 2.5-FeZ is *ca.* 140.2 kJ/mol. These results confirm that 8-FeZ has higher catalytic reactivity than 2.5-FeZ in the reaction.

The reusability of 8-FeZ in the benzylation of benzene with BC was tested. The reused catalyst was obtained by separating from reaction solution and then calcined at 550 °C for 5 h. It can be seen in Table 1, 8-FeZ could keep high conversion of BC (>90%) with 100% selectivity of DPM even after three reactions ran. Such catalytic performance is important for the potential industrial application. On the other hand, the catalytic reactivity of 8-FeZ in the benzylation of substituted benzene (toluene or *p*-xylene) with BC was also investigated. 8-FeZ showed high catalytic reactivity in the benzylation of substituted benzene (Table 1).

XRD patterns of these catalysts, Fe_2O_3 and HZSM-5 were collected by Rogaku Rotflex D/Max-C powder X-ray diffractometer with Cu Kα radiation (λ = 0.15046 nm) operated at 40 kV and 30 mA (Fig. 3). XRD characteristic peaks of HZSM-5 were observed on 8-FeZ and 2.5-FeZ, indicating that the Fe loading could not significantly change the framework of HZSM-5. However, XRD peaks of HZSM-5 detected in these catalysts slightly shifted toward the high 2θ (°) with respective to XRD peaks of zeolite HZSM-5. These results further indicate that the interaction of Fe