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

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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

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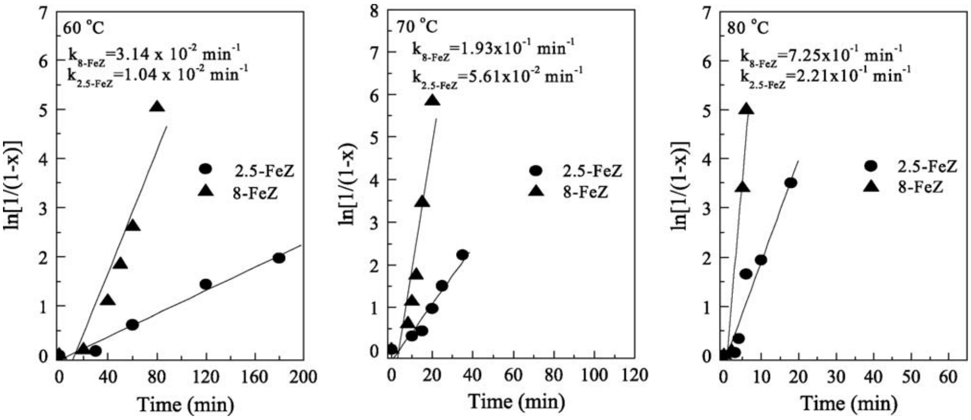

Fig. 1. Pseudo 1st order plots of benzylation of benzene with benzyl chloride on 2.5-FeZ and 8-FeZ catalysts at different temperature.

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

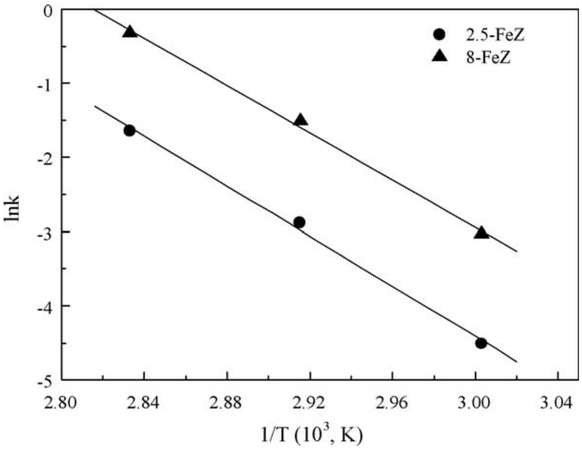

Fig. 2. Arrhenius plots of benzylation of benzene with benzyl chloride on these catalysts.

Table 1
Benzylation of different aromatic compound with BC on 8-FeZ catalyst.

Acromatic substrate	Runs	Conv. BC (mol%)	Sele. Product (mol%)	$T_{>90}$ (min)
Benzene	Fresh	98.8	Diphenylmethane (100%)	5
	First reuse	99.6	Diphenylmethane (100%)	5
	Second reuse	98.5	Diphenylmethane (100%)	7
Toluene	Fresh	100	*para*(*ortho, meta*)-Benzylated (100%)	5
p-Xylene	Fresh	100	2,5-Di methyl diphenylmethane (100%)	10

Reaction condition: 30 mL aromatic compound, 2.7 mL benzyl chloride, 0.2 g catalyst, 80 °C, reaction time = 3 h. $T_{>90}$: time required for more than 90% conversion of BC.

with HZSM-5 occurs on these catalysts. XRD peaks belonging to Fe oxides could not be found on 2.5-FeZ, suggesting that Fe species might be highly dispersed and isolated on the catalyst. 8-FeZ showed low intensity of the XRD peaks relative to 2.5-FeZ, and 8-FeZ presented weak broad XRD peaks belonging to Fe_2O_3. Hence, the dispersion of Fe species decreased and a little superfine Fe_2O_3 formed on 8-FeZ.

UV–vis spectra of these catalysts dispersed well in deionized water were recorded by Schimadu UV–vis 256 instrument (Fig. 4). Fe_2O_3 showed two broad bands at *ca*. 300 and 600 nm, belonging to Fe^{3+}–O^{2-} in bulk Fe_2O_3 [5]. Both 2.5-FeZ and 8-FeZ exhibited a shoulder peak at *ca*. 235 nm, tentatively assigned to the charge transfer between isolated Fe^{3+} and O^{2-} attached the framework of HZSM-5 [5,6]. 8-FeZ appeared a peak at *ca*. 305 nm, possibly due to

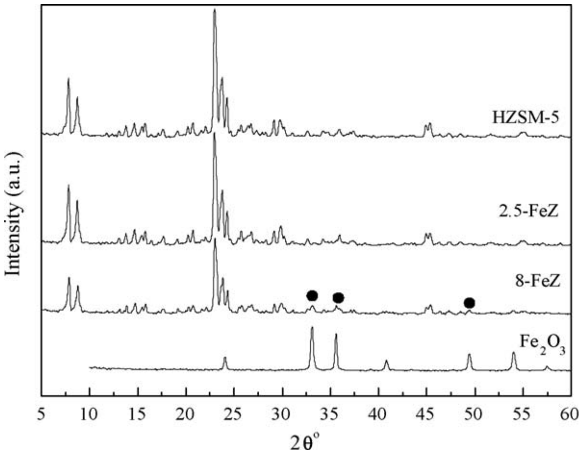

Fig. 3. XRD patterns of these catalysts.

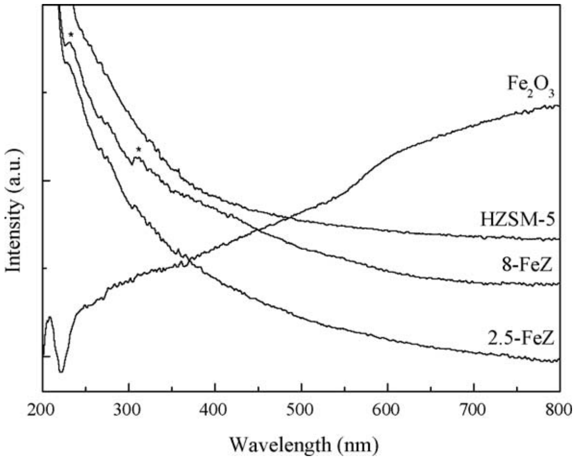

Fig. 4. UV–vis spectra of these catalysts.

the presence of Fe_2O_3 particles in the catalyst. Therefore, isolated Fe^{3+} species and Fe_2O_3 located in 8-FeZ. The result is agreement with that of XRD.

Benzylation of benzene with benzyl chloride is electrophilic substitute reaction [1–5,7]. The possible reaction mechanism has been proposed. Active metal ions (Me^{n+}) firstly attack benzyl chloride to form carboncation C_6H_5–CH_2^+ and $Me^{(n-1)+}$ through oxidation process; subsequently, benzene without activation directly reacts with C_6H_5–CH_2^+ to produce diphenylmethane, which is rate determining step [1,2,7]. In case of this work, the interaction of Fe with HZSM-5 induced the formation of isolated Fe^{3+} species on 8-FeZ and 2.5-FeZ catalysts. 8-FeZ and 2.5-FeZ exhibited high catalytic reactivity in the benzylation of benzene with benzyl chloride in comparison with Fe_2O_3 and HZSM-5. Therefore, isolated Fe^{3+} species are close relative to the catalytic reactivity of 8-FeZ and 2.5-FeZ. Fe_2O_3 had no significant activity in the reaction, possibly due to the shortage of isolated Fe^{3+} species.

8-FeZ had lower activation energy and higher rate constant than 2.5-FeZ, indicating that 8-FeZ possessed more active sites than 2.5-FeZ. On the other hand, the previous works revealed that the nano-particle Fe oxide could activate benzene to form C_6H_5–H ($C_6H_5^{\delta-}\cdots\cdots H^{\delta+}$) species which more easily reacted with C_6H_5–CH_2^+ than benzene [4,5,7]. Hence, the presence of a little superfine Fe_2O_3 on 8-FeZ enhanced the activation of benzene and favored the rate determining step in the benzylation of benzene with benzyl chloride. The isolated Fe^{3+} species and superfine Fe_2O_3 occurred synergistic catalysis to improve the catalytic reactivity of 8-FeZ. In summary, 8-FeZ exhibited higher catalytic reactivity than 2.5-FeZ in the benzylation of benzene with BC, due to the occurrence of synergistic catalysis between isolated Fe^{3+} species and Fe_2O_3 on 8-FeZ. Under the reaction conditions of 30 mL benzene, benzene/BC = 14.36 (mol ratio), 80 °C, 0.2 catalyst and reaction time = 5–7 min, the high conversion of BC with 100% selectivity of DPM was achieved on 8-FeZ catalyst even after three reactions ran. In addition, 8-FeZ showed good catalytic reactivity in the benzylation of substituted benzene (toluene, *p*-xylene) with BC.

Acknowledgments

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