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An efficient catalyst Fe$_2$O$_3$/HY for Friedel-Crafts acylation of

m-xylene with benzoyl chloride

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Abstract: Iron oxide supported on HY zeolite was prepared and exhibited excellent catalytic performance in the acylation of *m*-xylene with benzoyl chloride. It was characterized by XRD, BET, XPS, NH$_3$-TPD and Py-IR. The obtained results indicated that the catalytic activity of Fe$_2$O$_3$/HY is enhanced with the increase of Lewis acidic sites. Furthermore, the reaction parameters, including load of Fe$_2$O$_3$, temperature, molar ratio and the dose of catalyst, were optimized. Thus the acylation proceeds effectively to afford 2, 4-dimethylphenylacetophenone in 94.1% yield under optimum conditions. Finally, the catalyst was examined for the acylations of a series of arenes, all of the alkyl substituted benzenes were transformed to the corresponding products in satisfied yields while the acylation of chlorobenzene was sluggish. The catalyst was easily separated from the reaction mixture and reused five runs without appreciable loss of catalytic activity.

**Key words:** Acylation, *m*-Xylene, Benzoyl chloride, Iron oxide, HY zeolite

1. Introduction

Friedel-Crafts acylation of arenes is considered as an important way for production of aromatic ketones, which are the key intermediates or final products in pharmaceutical, agrochemical and cosmetic industry[1-3]. Traditionally, Lewis acids (such as AlCl$_3$, FeCl$_3$, TiCl$_4$ and BF$_3$) or strong Brönsted acids (such as concentrated H$_2$SO$_4$) are required as the vital catalyst for this reaction. However, these catalysts normally suffer from highly toxic, corrosive, and discarding a large amount of waste water[4]. Recently, zeolite[5,6]、clay[7]、Nafion-H[8]、sulfated zirconia[9] and Keggin-type heteropolyacid[10] as solid acid catalysts are widely used in Friedel-Crafts acylations.

Nowadays, metal oxide especially iron oxide as catalysts have been widely used for various reaction, such as oxidation[11] and hydrogenation[12, 13], but little research was reported on the Friedel-Craft acylation. Moreover, Zeolites, well-known microcrystalline porous materials, exhibit Lewis and Brönsted acidity, thermal stability, shape selectivity and ease to separation. Chiche and co-workers firstly reported the acylation of toluene with aliphatic acids over CeNaY zeolite. This catalyst showed an extroardinary high *para* shape-selectivity. However, the reactions

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required severe reaction conditions and gave poor yields[14]. Recently, V. N. Sheemol[15] reported that the catalytic activity can be improved by the modification of H-Beta zeolite with simple cation exchange (La^{3+}, Ce^{3+}, Dy^{3+}). Moreover, Laidlaw and co-workers[16] claimed that Zn- and Fe-exchanged zeolites (HZSM-5, HY and mordenite) for toluene benzoylation are more effective than the original zeolites. They also discovered that Fe-exchanged zeolites gave limited leaching of Fe cations into solution compared to other metal cations. Nowadays, catalyst deactivation was the main hindrance in the large-scale industrial applications of modified zeolite catalysts[17].

Thus, in the present work, several metal oxides supported on HY zeolite were examined for the acylation of *m*-xylene with benzoyl chloride (Scheme 1), and the best catalytic performance was displayed by Fe_2O_3/HY. These catalysts were comparatively characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), NH_3-temperature programmed desorption (TPD) and IR spectra of adsorbed pyridine (Py-IR). The influence of the Si/Al ratio (SAR) of the support was evaluated. Additionally, the reaction parameters such as load of Fe_2O_3, temperature, molar ratio of the reactants and the dose of catalyst were also optimized.
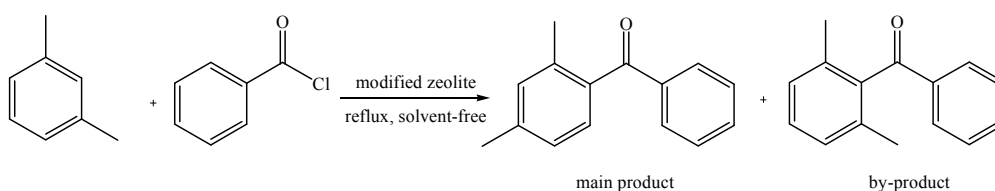
Scheme 1 Acylation of *m*-xylene with benzoyl chloride

2 Experimental

2.1 Materials and Catalysts

The zeolites, HY (Si/Al=7、9、11), HBeta (Si/Al=25), ZSM-5 (Si/Al=25) and Mordenite, were purchased from Nankai University Catalyst Co., Tianjin, China. *m*-Xylene (AR) and benzoyl chloride (AR) were obtained from Tianjin Guangfu Fine-chemical institute, Tianjin, China. Commercially available reagents were used without further purification.

The catalysts used in this study were prepared by the equal-volume impregnation method. For example, Fe_2O_3/HY was prepared as follows. HY zeolites (10 g) were impregnated with 10.0 mL aqueous solution of 1.5 g iron nitrate hexahydrate (15

wt%). After impregnating at ambient temperature for 4 h, it was dried at 110 ℃ for 5 h and calcined at 550℃ for 5h. Several metal oxides (CoO, NiO, LaO, CeO and Al_2O_3) supported on HY zeolite were prepared by the same method. Furthermore, Fe_2O_3/HY catalysts with different Fe_2O_3 loads were also prepared and hereinafter referred to as xFe_2O_3/HY (x = 10-20%).

2.2 Characterization

The crystallinity of catalysts was determined by X-ray powder diffraction with Rigaka D/max 2500 X-ray diffractomater using Cu-K_α radiation (40kV, 100mA) in the range of 5~90℃. The specific surface areas were determined by the BET method with N_2 adsorption-desorption measurements at liquid nitrogen temperature using a NOVA 2000e analyzer. IR spectra were obtained using the KBr method on a Nicolet system. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI1600 spectrometer with a Mg Ka X-ray source for excitation. NH_3-TPD was conducted with a ChemiSorb 2750 instrument at an atmospheric pressure with a thermal conductivity detector device. The IR spectra of adsorbed pyridine were recorded on a Thermo Nicolet Nexus 470 spectrometer equipped with a heatable and evacuatable IR cell containing CaF_2 windows.

2.3 General procedures for the acylation of *m*-xylene with benzoyl chloride

A mixture of *m*-xylene (40 mmol), benzoyl chloride (10 mmol) and catalyst (70 mg, 5 wt%) was magnetically stirred and heated to reflux (130℃）for 5h. The catalyst was separated from the reaction mixture by simple filtration and then the filtrate was analyzed by gas chromatography (SE-30 capillary column: 60m×0.25mm, 0.2 um film thickness) and the composition of the reaction mixture was confirmed by GC-MS (HP-1 capillary column: 30m×0.25mm, 0.2 um film thickness).

3. Results and discussion
3.1 Catalyst selection

As mentioned above, solid acids were intensively studied for the alkylation and acylation of arenes recently. Thus, several zeolites, including HY, HBeta, ZSM-5 and Mordenite were firstly selected as catalysts for the acylation of *m*-xylene with benzoyl chloride in this study. The obtained results were summarized in Table 1 (entry 1-4). It was obvious that these zeolite catalysts presented low activity, the conversion of *m*-xylene were all less than 30.0%. This is possibly attributed to the weak Lewis

acidity of zeolites. Therefore, in order to enhance the Lewis acidity of catalysts, several metal oxides were doped into HY zeolite, the obtained catalysts were examined for the above reaction, and the results were presented in Table 1 (entry 5-10). The experimental results showed that Fe_2O_3/HY catalyst displayed much better catalytic performance than the other catalysts, the conversion of m-xylene was 97.3%. Therefore, Fe_2O_3/HY was chosen as the catalyst for the following study. To further understand these results, these catalysts were studied by NH_3-TPD, Py-IR and XRD.

Table 1 Catalytic performance of catalysts in the acylation of m-xylene with benzoyl chloride

Entry	Catalyst	Conversion[a] (%)	Selectivity[b] (%)	Yield (%)
1	HY	30.37	82.52	25.06
2	Mordenite	27.06	73.59	19.91
3	HZSM-5	23.50	68.42	16.08
4	HBeta	16.49	81.29	13.40
5	Fe_2O_3/HY	97.29	93.74	91.20
6	NiO/HY	89.95	91.70	82.48
7	CoO/HY	72.56	94.69	68.71
8	Al_2O_3/HY	37.55	80.04	30.06
9	CeO/HY	-	-	-
10	LaO/HY	-	-	-

Reaction condition: m-xylene : benzoyl chloride= 4:1; the amount of catalyst = 5 wt%; T=130℃

[a] The conversion of benzoyl chloride

[b] The selectivity of 2,4-dimethylphenyl- acetophenone

3.2 Characterization

3.2.1 NH_3-TPD and Py-IR

In this study, extensive NH_3-TPD studies were performed to compare the acidity distinction between HY and Fe_2O_3/HY and the TPD curves were shown in Fig. 1. Both of them exhibited three typical desorption peaks, which could be assigned to the

weak (50-150 ℃, T_1), medium (150-300 ℃, T_2) and strong acid sites (300-600 ℃, T_3), respectively. It was obvious that the desorption temperature on the weak acid sites increased with iron oxide introduction. Therefore, the strength of the weak acid sites on Fe_2O_3/HY was apparently higher than that of HY catalyst. Furthermore, the area of a specific peak could be used to estimate the amount of ammonia desorbed from the sample and taken as a standard to quantify the acid capacity of the sample [18]. As summarized in Table 2, the total acid capacity of Fe_2O_3/ HY is a little higher than that of HY catalyst while its strong acid capacity is less than HY.
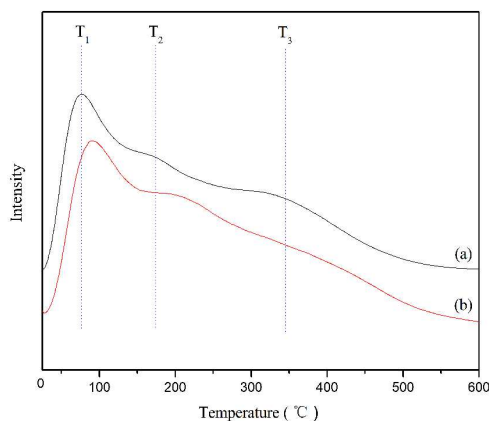
Fig. 1. NH_3-TPD curves for (a) HY, (b) Fe_2O_3/ HY

Table 2 Acid capacity of two catalysts

Catalysts	Low temperature Peak area [a. u.]	Medium temperature Peak area [a. u.]	High temperature Peak area [a. u.]	Total Peak area [a. u.]
HY	2.2690	3.6477	6.9408	12.8575
Fe_2O_3/ HY	2.7915	4.5259	5.8038	13.1212

To get further information about the Brönsted and Lewis acid sites, Py-IR spectra of HY and Fe_2O_3/HY were performed (Fig. 2). The bands at 1540 cm^{-1} and 1450 cm^{-1} were attributed to the pyridine adsorbed on the Brönsted and Lewis acid sites, respectively[19]. The integrated areas for Brönsted and Lewis acid sites were obtained and the calculated L/(L+B) ratios were listed in Table 3. The results demonstrated that both the amounts of Lewis acid sites and L/(L+B) ratio increase remarkably by doping Fe_2O_3 into HY zeolite. This result obviously revealed that Lewis acid sites are more important than Brönsted acid sites for the acylation of *m*-xylene with benzoyl chloride. This is the possible reason that Fe_2O_3/HY exhibited excellent catalytic activity. Based on the analysis from Fig. 2 and Table 3, we could conclude that the

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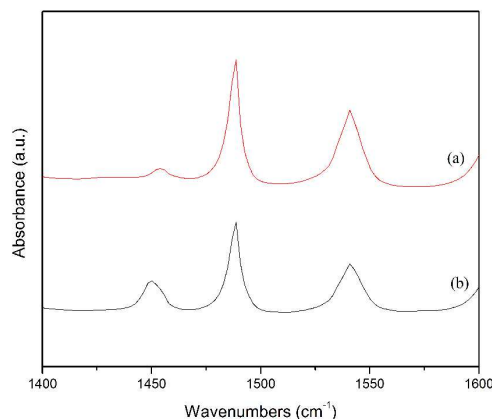conversion of *m*-xylene was improved with the increase of Lewis acid sites.

Fig. 2. Py-IR spectra of (a) HY and (b) Fe$_2$O$_3$/HY

Table 3. Integrated areas for Brönsted and Lewis acid sites in FT-IR spectra of adsorbed pyridine on HY and Fe$_2$O$_3$/HY catalysts

Catalysts	Integrated areas [a]		L/(B+L) ratio
	Brönsted	Lewis	
HY	46.03	23.99	0.34
Fe$_2$O$_3$/HY	42.91	29.88	0.41

[a] Integrated areas of Lewis and Brönsted acid sites were based on band at 1450 cm^{-1} and 1540 cm^{-1}, respectively

3.2.2 Textural properties of catalysts

The specific surface areas and pore structural parameters of HY and Fe$_2$O$_3$/HY are summarized in Table 4. In comparison with HY zeolite, the total and micropore surface area of Fe$_2$O$_3$/HY decreased a little. Meanwhile, there was no significant change for the pore size. It was obvious that the morphology structure of HY was almost unchanged by doping Fe$_2$O$_3$ into HY catalyst. Nevertheless, Fe$_2$O$_3$/HY exhibited better catalytic activity than HY zeolite (see Table 1), this indicated that iron oxide in Fe$_2$O$_3$/HY play an important role as the active species in the acylation of *m*-xylene with benzoyl chloride.

Table 4 Textural properties of the catalysts

Samples	Surface area (m^2/ g)		Pore volume[b] (cm^3/ g)	Average pore diameter[a] (Å)
	Total	Micropore[a]		
HY	663.2	619.1	0.36	1.09
Fe$_2$O$_3$/ HY	649.9	585.9	0.37	1.14

3.2.3 XRD

The XRD patterns of HY and Fe_2O_3/HY were shown in Fig. 3. All samples exhibited the typical diffraction peaks of the faujasite (FAU) structure. However, the intensity of the peaks for Fe_2O_3/HY decreased slightly. It was probably due to the change in the crystallinity when Fe_2O_3 was distributed on the HY surface[20, 21]. Furthermore, the diffraction spectra of Fe_2O_3 could not be observed on the XRD patterns of Fe_2O_3/HY catalyst. The results suggested that Fe_2O_3 species were either in the amorphous form or highly dispersed as very small particles on HY zeolite. Similar phenomena were reported for TiO_2 supported on HY and iron supported on mesoporous silica [22, 23].
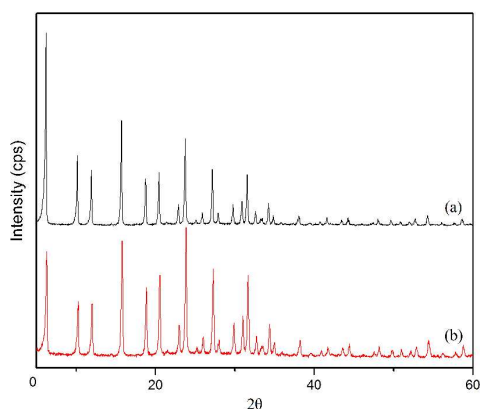
Fig. 3. XRD patterns of (a) HY and (b) Fe_2O_3/ HY

3.2.4 XPS

The XPS spectra of Fe_2O_3/HY catalyst was presented in Fig. 4. The typical Fe 2p XPS narrow scan spectrum presented two main peaks at about 711.5 and 724.0 eV corresponding to the spin-orbit split doublet of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ (Fig. 4(b)), which implied that the iron element on the catalyst surface existed mainly in the form of Fe^{3+} species. The O1s XPS of the sample showed a single peak at 532.2 eV corresponding to the oxide oxygen (O^{2-}) in Fe_2O_3(Fig. 4(a)). Therefore, these results indicated that the Fe species were predominantly in the form of Fe_2O_3.
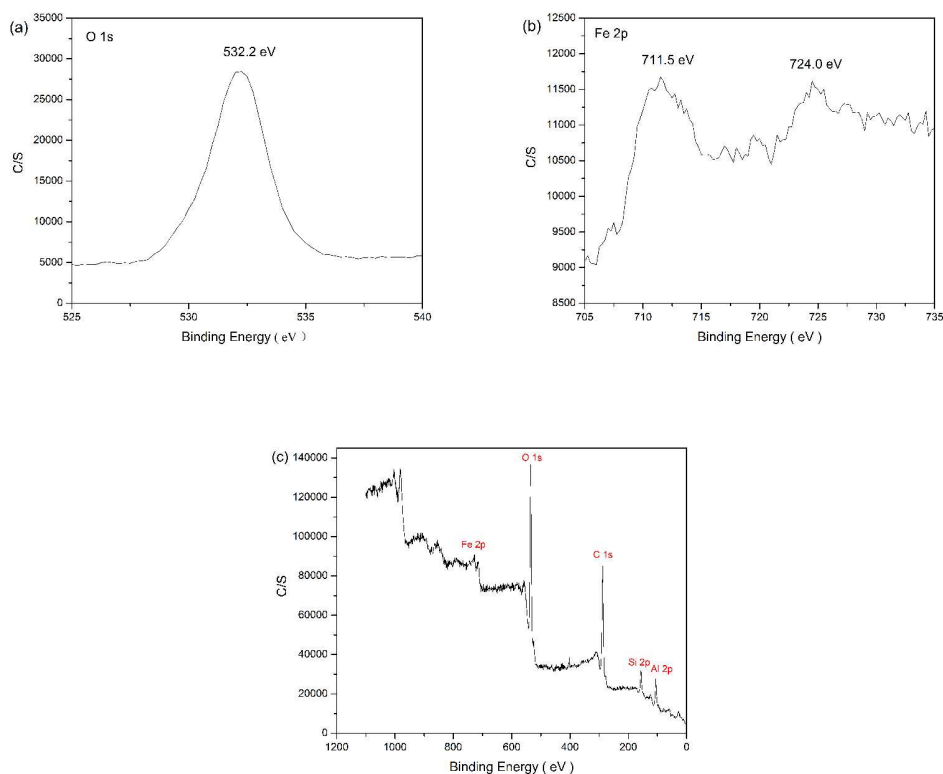
Fig. 4. XPS spectra of Fe_2O_3/ HY catalyst

3.3 The effect of Fe_2O_3 load in Fe_2O_3 / HY

The effect of Fe_2O_3 load on the acylation of *m*-xylene with benzoyl chloride was investigated and the results were described in Fig. 5. With the increase of Fe_2O_3 load from 10 to 15 wt%, the conversion of benzoyl chloride increased rapidly. According to the above discussion, with the increase of Fe_2O_3 load, Lewis acidic sites increase, led to enhance the activity of Fe_2O_3/HY. However, when the load reached to 20 wt%, the conversion of benzoyl chloride displayed a slight drop as compared to 15 wt% load at the same reaction conditions. Thus $15Fe_2O_3$/HY was selected for the acylation of *m*-xylene with benzoyl chloride.
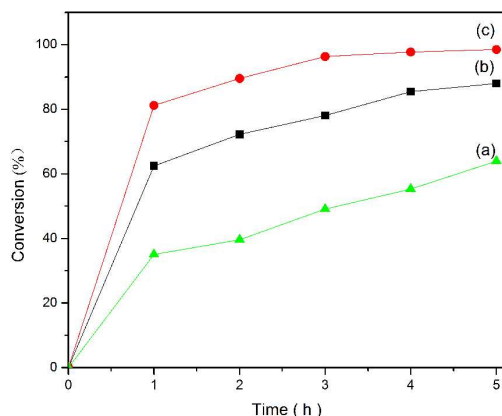
Fig. 5. Influence of Fe_2O_3 load on the conversion of benzoyl chloride. *m*-xylene : benzoyl chloride= 4:1; catalyst dose = 5 wt%; T= 110 ℃. (a) 10 wt%, (b) 15 wt%, (c) 20 wt%.

3.4 The effect of Si/Al ratio of HY zeolite

Some researchers reported that the catalytic activity of zeolites on Friedel-Craft acylation was influenced by the Si/Al ratio (SAR) of zeolite[24]. Thus, the effect of the SAR of HY support on the acylation of *m*-xylene with benzoyl chloride was examined and the results are listed in Table 5. It was obvious that the conversion of benzoyl chloride increased from 79.39% to 99.58% when the framework SAR value of HY zeolite decreased from 11 to 7. This was mainly due to the increase of the total Lewis acid sites with decrease of the SAR value of HY support, and then the increase of the catalytic activity was observed.

Table 5 Effect of Si/Al ratio of HY zeolite to the reaction

Entry	Catalyst	Conversion（%）	Selectivity（%）	Yield（%）
1	Fe_2O_3/ HY(Si/Al= 7)	99.58	94.48	93.88
2	Fe_2O_3/ HY(Si/Al= 9)	80.63	95.31	76.85
3	Fe_2O_3/ HY(Si/Al= 11)	79.39	89.12	70.75

Reaction condition: *m*-xylene : benzoyl chloride= 4:1; catalyst dose = 5 wt%; T=130 ℃

3.5 The effect of reaction parameters

The acylation of *m*-xylene with benzoyl chloride over Fe_2O_3/HY was examined

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at a temperature range from 70 to 130℃ and the results are shown in Fig. 6a. As the temperature increased, the conversion of benzoyl chloride increased sharply during 70-110 ℃ and then increased slightly above 110 ℃. Thus, reflux temperature (130 ℃) was chosen as the optimum reaction temperature.

The influence of the amount of catalyst on the conversion of benzoyl chloride was investigated ranged from 2 wt% to 8 wt%. It was found that the conversion of benzoyl chloride increased from 89.2% to 99.6% with an increase of the amount of catalyst from 2 to 5 wt% (Fig. 6b). Further increase to 8 wt%, no appreciable effect was observed on the conversion of benzoyl chloride. Thus, 5 wt% was selected to be the suitable catalyst amount.

The effect of molar ratio of *m*-xylene and benzoyl chloride to the acylation was studied over Fe_2O_3/ HY catalyst and the results were described in Fig. 6c. At a molar ratio of 1, the conversion of benzoyl chloride was only 47.1%. With the increase of the molar ratio from 1 to 4, the conversion of benzoyl chloride remarkably increased because the excess of *m*-xylene would enhance the transformation of benzoyl chloride. Thus, the molar ratio of *m*-xylene to benzoyl chloride was selected as 4.
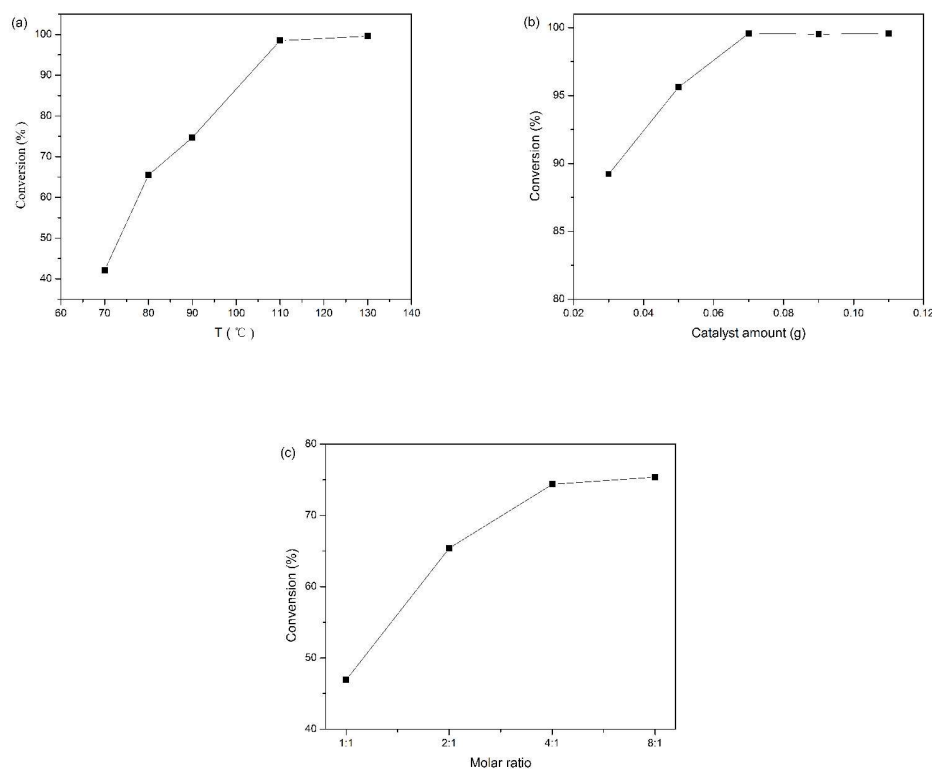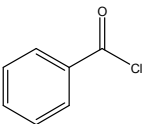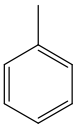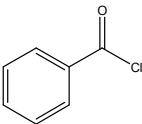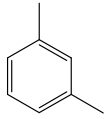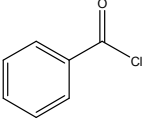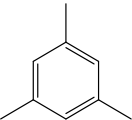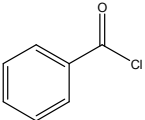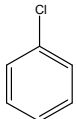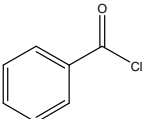

Fig. 6 (a). Influence of reaction temperature on the conversion of benzoyl chloride.*m*-xylene :

benzoyl chloride= 4:1; catalyst dose = 5 wt%. (b). Influence of catalyst amount on the conversion of benzoyl chloride. m-xylene : benzoyl chloride= 4:1; T= 130 ℃. (c) Influence of molar ratio of m-xylene/ benzoyl chloride on the conversion of benzoyl chloride. catalyst dose = 5 wt%; T= 90 ℃.
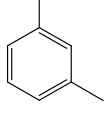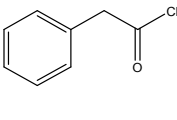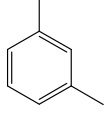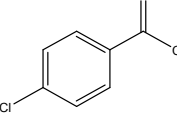
As mentioned above, Fe_2O_3/ HY catalyst displayed excellent catalytic activity in the acylation of m-xylene with benzoyl chloride. Therefore, the study was extended to the Friedel-Crafts acylation reaction of benzoyl chloride with several aromatic compounds having different substituents, including benzene, toluene, m-xylene, mesitylene and chlorobenzene. Reactions were carried out under the optimum reaction conditions and the results are summarized in Table 6 (entry1-5). As expected, the benzoylation of mesitylene proceeded more effectively than m-xylene due to the presence of more electron donating groups. This result was quite consistent with the conventional Friedel-Crafts acylation reactions[1]. Howerver, chlorobenzene was sluggish in the acylation and the conversion was low since the electron withdrawing nature of chloro group. Furthermore, Fe_2O_3/ HY was employed in the acylations of m-xylene with phenylacetyl chloride and 4-chlorobenzoyl chloride, respectively (Table 6, entry 6, 7). It was found that the conversion of benzoyl chloride was 99.5%, while that of 4-chlorobenzoyl chloride was 91.5% at the same reaction conditions. This was mainly due to the synergistic effect of electron withdrawing induction and donating conjugation of chloride atom. Moreover, the conversion of phenylacetyl chloride was slightly lower than that of benzoyl chloride. It was attributed to the difficulty of forming phenylacetyl cation.

Table 6. Influence of various substrates or acylation reagents on acylation reaction

Entry	Substrate	Acylation reagent	Time (h)	Temperature (℃)	Conversion (%)	Yield (%)
1			5	80	14.58	6.33
2			10	110	66.68	43.20

3			5	130	99.58	93.39
4			3	110	100	100
5			10	130	-	-
6			5	130	95.39	74.74
7			5	130	91.48	87.49

3.6. Reusability of the catalyst

The separation and reusability of catalysts are quite important for acylations. So the recycling experiments were performed over Fe_2O_3/HY and the results are presented in Fig. 7. The catalyst was separated from the reaction mixture by simple filtration, washed with ethanol and reused after drying at 110 ℃ for 5h. It was seen from Fig. 7 that the conversion of benzoyl chloride displayed a slight drop after the third run. The decrease of benzoyl chloride conversion was probably attributed to the unavoidable trace mechanical loss of catalyst during work-up procedures. These results indicated that Fe_2O_3/ HY catalyst exhibited excellent stability, no significant deactivation of Fe_2O_3/ HY catalyst was detected during its reuse in the acylation.

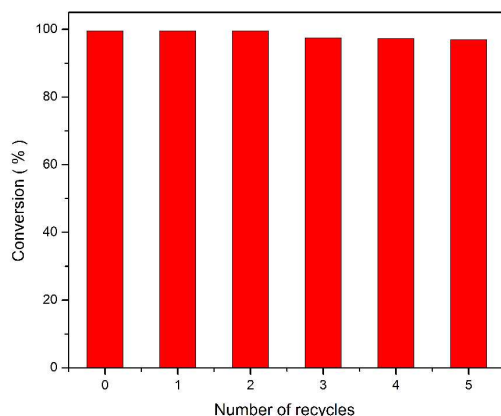Fig. 7. Reusability of Fe_2O_3/ HY catalyst. *m*-xylene : benzoyl chloride= 4:1; catalyst dose = 5 wt%;
T= 130 ℃

Moreover, the acylation of *m*-xylene with benzoyl chloride over Fe_2O_3 would be a homogeneously catalysed reaction. It would result in the formation of the soluble compound $FeCl_3$, which was powerful homogeneous Friedel-Crafts catalyst. However, the obtained result indicated that the Friedel-Crafts acylation over Fe_2O_3/ HY would be a well heterogeneously catalysed reaction. It could be due to the strong interaction of Fe_2O_3 with HY zeolite, which inhibited the reaction of Fe_2O_3 with benzoyl chloride.

4. Conclusions

In summary, iron oxide supported on HY zeolite was found to be an efficient, stable and reusable solid acid catalyst for Friedel-Craft acylation reaction and exhibited excellent catalytic performance in the acylation of *m*-xylene with benzoyl chloride. 99.5% Conversion of benzoyl chloride and 94.5% selectivity of 2,4-dimethylphenyl-acetophenone were achieved. The catalysts were characterized by XRD, BET, XPS, NH_3-TPD, Py-IR and the results revealed that the catalytic activity of Fe_2O_3/HY was enhanced by the increase of Lewis acidic sites. Furthermore, it was found that the catalytic acitivity increased with the SAR decrease of HY zeolite. The influences of iron oxide load, temperature, molar ratio and catalyst dose were investigated and optimized. The reusability tests of the catalyst showed that this catalyst can be used five runs without appreciable loss in catalytic activity.

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