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1. Introduction

Cyclohexanol is used widely to produce adipic acid, caprolactam, hexamethylene diamine and cyclohexanone.¹ The main processes for the production of cyclohexanol are based on the oxidation of cyclohexane,^{2,3} the hydrogenation of phenol,¹ and the direct hydration of cyclohexene.⁴ The cyclohexane oxidation process is used mainly in industry, but it is hazardous. And phenol hydrogenation, as the oldest method of cyclohexanol production, is subject to greater restrictions in industrial application due to the high cost of raw materials and the consumption of large amounts of hydrogen and energy. In addition, although direct hydration is highly selective, increasing economic benefits to a certain extent and reducing the possibility of danger in the two traditional production processes, it allows only a very low conversion per pass, because of slightly exothermic and equilibrium limited.⁵

To overcome the main problem of the thermodynamic equilibrium limitation of the direct hydration reaction of cyclohexene, the indirect hydration of cyclohexene was born out, which is a two-step process using formic acid as a reactive entrainer.⁶⁻⁹ In the first step, cyclohexene react with formic acid to produce cyclohexylformate, which is an electrophilic addition esterification,¹⁰ needing acid catalyst to increase the conversion rate of cyclohexene. In the second step, the ester readily hydrolyzes to produce cyclohexanol. Steyer *et al.*^{5,6,11}

Comparative research on three types of MIL-101(Cr)-SO₃H for esterification of cyclohexene with formic acid

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MIL-101(Cr)-SO₃H was prepared by a one-pot synthesis method using CrO₃ or Cr(NO₃)₃'9H₂O as a Cr source and 2-sulfoterephthalic acid monosodium salt as a ligand with three different mineralizers, HCl, HF and NaAC, respectively. Among the prepared catalysts, MIL-101(Cr)-SO₃H, which uses HCl as a mineralizer, has a high specific surface area and the strongest acidity compared with the other two mineralizers. When these catalysts were used to catalyze the esterification of cyclohexene with formic acid, MIL-101(Cr)-SO₃H prepared using HCl as a mineralizer possessed the highest catalytic activity in the esterification, because the conversion rate of cyclohexene is 63.97%, whereas MIL-101(Cr)-SO₃H prepared using NaAC and HF as a mineralizer shows cyclohexene conversion rates of 38.40% and 32.46%, while their selectivity to cyclohexyl formate is about 97.50%. MIL-101(Cr)-SO₃H with HCl as a mineralizer can be reused three times in succession without any loss of catalytic activity.

simulates the indirect hydration process using two distillation towers. Sulfonic-acid resin Amberlyst-15 catalyzed the esterification of cyclohexene with formic acid in the first distillation tower, the hydrolysis of cyclohexyl formate occurred in the second column. Cyclohexene conversion reached about 100%. But distillation tower costs highly, and sulfonic-acid resin Amberlyst-15 deactivates and swells easily. Imam et al.7 evaluated indirect hydration process, agreed that the energy consumption of the process is much lower than direct hydration process. Du et al.12 used HZSM-5 as catalysts in indirect hydration, and obtained cyclohexanol yields of up to 40%, which was far more than in the direct hydration of cyclohexene, and HZSM-5 could be reused without apparent inactive. Previous studies have shown that the hydrolysis reaction of ester occurs easily, the addition esterification of cyclohexene with formic acid by acid catalyst is the key step to realize the indirect hydration.5

Sulfonic acid is a very strong organic acid, which acidity is similar to that of general inorganic acids. Sulfonic-acid resin Amberlyst-15 (ref. 13) worked well, but it swelled and could not be reused. The introduction of sulfonic groups into inorganic carriers has attracted the attention of researchers. There are a number of sulfonic acid functionalized catalysts are used in acid-catalyzed reactions, and performed successfully great catalytic activity and recyclability, including cellulose hydrolysis reaction,¹⁴ heterogeneous alcoholysis reaction,¹⁵ acetal reaction,¹⁶ partial esterification reaction.^{17,18} Among them, SBA-15-SO₃H^{19,20} can be reused to some extent in some acid-catalyzed reactions, but the grafted sulfonic-acid group is limited because of the limited content of Si–OH on the carrier of the SBA-15 molecular sieve. Furthermore, the distribution of





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sulfonic-acid groups is not uniform, which results in the reaction solution not being in sufficient contact with the active component during the reaction.

Metal–organic frameworks (MOFs),^{17,18,21,22} as porous crystalline materials, have high specific surface area, large pore volume, and the advantages of more regular structure and easy modification by functional organic ligands. Since Férey prepared successfully MIL-101(Cr) using HF as mineralizer that can not only increase the solubility of terephthalic acid in solvent but also regulate the nucleation rate of catalysts,²³ many researchers began to notice its prominence. MIL-101(Cr) has higher specific surface area and larger pore volume than other MOFs, and it overcomes the disadvantages of poor thermal and chemical stability of other MOFs,^{23–25} which make it a focus. Huang *et al.*²⁶ synthesized MIL-101(Cr) by NaAC as mineralizer, and discovered that it had better thermostability than prepared by HF as mineralizer.

According to that MIL-101(Cr)^{23,26} can be prepared by different mineralizers and resulted in different performance, we synthesized MIL-101(Cr)-SO₃H by HF, NaAC as mineralizer, respectively. In addition, George Akiyama prepared MIL-101(Cr)-SO₃H using HCl as mineralizer, which showed high durability to boiling water and distinct and clean catalytic activity for the cellulose hydrolysis reaction, with a strong Brønsted acid site on its pore surface.¹⁴ And we also used HCl to synthesize MIL-101(Cr)-SO₃H. We just researched *in situ* synthesis method, because the catalytic activity of MIL-101(Cr)-SO₃H prepared by the post-modification method is inferior to the one-step synthesis of MIL-101(Cr)-SO₃H.¹⁸ In addition, these three types of MIL-101(Cr)-SO₃H were catalyzed the esterification of cyclohexene with formic acid for the first time.

2. Experimental section

2.1 Materials and chemicals

All solvents and reactants were from commercially available sources and were used without further purification. Chromium nitrate nonahydrate, chromium oxide, terephthalic acid, fomic acid and cyclohexene (AR, 98%) were from Macklin (China). Hydrofluoric acid (AR, 40%), 37% fuming hydrochloric acid, sodium acetate, concentrated sulfuric acid (AR, 98%), ethanol and acetone were from Sinopharm Chemical Reagent Co., Ltd (China). Monosodium 2-sulfoterephthalic acid was from TCI (Shanghai) Development Co., Ltd., respectively.

2.2 Catalyst preparation

2.2.1 MIL-101-SO₃H_{HCl} synthesis. According to the procedure by Akiyama and co-workers,¹⁴ a mixture of monosodium 2-sulfoterephthalic acid (2 g, 7.5 mmol), CrO_3 (0.75 g, 7.5 mmol) and concentrated aqueous hydrochloric acid (12 N, 0.546 g) were dissolved in water (30 g), and the mixed solution was treated hydrothermally at 453 K for 6 d. The cooling prepared solid solution was washed three times each with ethanol and deionized water and after centrifugal separation and vacuum

drying for 6 h at 150 $^{\circ}\mathrm{C},$ the obtained green powder was denoted MIL-101-SO_3H_{HCl}.

2.2.2 MIL-101-SO₃H_{HF} synthesis. A mixture of chromium(III) nitrate nonahydrate (2.00 g, 5 mmol), monosodium 2-sulfoterephthalic acid (2.70 g, 10 mmol), deionized water (30 g) and hydrofluoric acid (47–51 wt%, 0.3 g) were heated for 24 h at 463 K. The cooling prepared solid solution was washed three times each with ethanol and deionized water and a green powder was obtained by centrifugal separation and vacuum drying for 6 h at 150 °C. The synthesized green powder was termed MIL-101-SO₃H_{HF}.²⁷ When we replaced monosodium 2-sulfoterephthalic acid with terephthalic acid, the resulting green powder was denoted MIL-101(Cr).

2.2.3 MIL-101-SO₃H_{NaAC} synthesis. A mixture of chromium(m) nitrate nonahydrate (2.00 g, 5 mmol), monosodium 2-sulfoterephthalic acid (2.70 g, 10 mmol), deionized water (30 g) and sodium acetate (0.12 g, 0.9 mmol) were heated at 463 K for 24 h. The cooling prepared solid solution was washed three times each with ethanol and deionized water and a green powder was obtained by centrifugal separation and vacuum drying for 6 h at 150 °C. The synthesized green powder was termed MIL-101-SO₃H(Na)_{NaAC}.

 $\rm MIL-101(Cr)-SO_3H(Na)_{NaAC}~(1~g)$ was added to 5 g 0.1 mol $\rm L^{-1}~H_2SO_4$ solution and 10 mL ethanol, stirred at room temperature for 24 h, and washed with ethanol until the washing solution became neutral. Finally, the green powder was dried in vacuum for 6 h at 150 °C.^{28} The resulting sulfonic acid-functionalized MIL-101 was termed MIL-101-SO_3H_{NaAC}.

2.3 Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a D/ Max-2500 diffractometer using Cu-Ka radiation from 2-14° with a step size of 0.02°. The textural properties of the prepared samples were outgassed for 4 h at 423 K and determined by N2 adsorption at 77 K, using a NOVA 2200e instrument (Quanta chrome, USA). The infrared (IR) spectra were collected on a Thermo Nicolet 380 Fourier transform infrared (FT-IR) spectrophotometer in KBr disks at room temperature. Thermal stability analysis was performed from 30 °C to 800 °C at 10 °C min⁻¹, using a TGA/DSC/1600HT analyzer (Mettler Toledo, Switzerland). The S content in the catalysts was measured by using an Elementar Vario EL III analyzer; and the Na and Cr contents were measured by Thermo Jarrell Asch IRIS Advantage 1000 inductively coupled plasma-atomic spectroscopy. The acid strength and the amount of acid on the catalysts was determined by ammonia-temperature-programmed desorption (NH₃-TPD), in which samples were programmed from 80 °C to 700 °C at 10°C min⁻¹. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A, Shimadzu group company) using a monochromatic Al K150 W X-ray source. The analysis chamber pressure was less than 5 \times 10⁻⁹ torr. An energy step size of 0.1 eV was chosen for the survey spectra. The BE scale was calibrated according to the C 1s peak (284.8 eV) of adventitious carbon on the analyzed sample surface. Peak fitting was carried out on the basis of Gaussian functions.



Scheme 1 Equation of the esterification of cyclohexene with formic acid over MIL-101(Cr)-SO₃H.

2.4 Esterification of cyclohexene with formic acid

Cyclohexene (4.11 g) and formic acid (6.90 g) were added sequentially to a three-necked round-bottom flask in a 1:3 molar ratio, and the amount of catalyst (0.55 g) used was 5% of the total mass of the reactants. The reaction mixture was stirred magnetically at 80 °C in an oil bath for 6 h. After the reaction, the solution was cooled to room temperature, an appropriate amount of acetone solvent was added to the threenecked flask, and the reaction liquid was mixed to a single phase by stirring for 30 min.19 The supernatant liquid sample was used to determine the conversion rate of cyclohexene and the selectivity of cyclohexyl formate by gas chromatography using an Agilent 7890 instrument with a HP-5 capillary column and FID indicator. The used catalyst was dried in vacuum at 423 K for 12 h, before being used in consecutive runs. The equation for the reaction of cyclohexene with formic acid is as shown in Scheme 1.

3. Results and discussion

3.1 Characterization of fresh catalyst samples

3.1.1 Nitrogen adsorption. N2 adsorption isotherms measured at 77 K (Fig. 1A) reveal two characteristic steps of the MIL-101-SO₃H that are related to the filling of the mesoporous and microporous cavities. The adsorption of MIL-101-SO3HNAAC increased most rapidly at all pressure stages, which indicates

that MIL-101-SO3H_{NaAC} contains more mesopores than the other two. And the pore-size-distribution curve of the different samples confirms the above discussion (Fig. 1B).16,29 The specific surface area and pore-diameter distribution of the samples is shown in Table 1. Based on a comparison of the parameters, the specific surface area of the MIL-101-SO₃H_{HF} is maximum, the specific surface area of MIL-101-SO3HNAAC and MIL-101-SO₃H_{HCl} are similar and a little smaller than MIL-101-SO₃H_{HF}, while their pore volume characteristics show that MIL-101-SO3HHF has most micropores and MIL-101-SO3HNAAC contains most mesopores.

3.1.2 FT-IR characterization. The FT-IR results of the different samples in Fig. 2 show that MIL-101-SO₃H and MIL-101(Cr) are essentially identical in their infrared characteristic peak positions. The characteristic peak of MIL-101(Cr)-SO₃H at 1182 cm^{-1} belongs to the antisymmetric vibration of O=S=O, whereas the symmetric stretching vibration occurs at 1228 cm⁻¹. The benzene ring skeleton vibration in-plane of the sulfonic acid substitution occurs at 1084 cm⁻¹, whereas 1024 cm⁻¹ is the strong stretching vibration of S-O and 623 cm⁻¹ is the stretching vibration peak of C-S.^{30,31} It can be concluded that the sulfonic acid groups were grafted successfully onto the MIL-101(Cr), regardless of which of the three mineralizers was used.

3.1.3 Elemental analysis. Table 2 shows that MIL-101-SO₃-H_{HCl} has the highest content of S and Cr and the least Na⁺, whereas MIL-101-SO₃H(Na)_{NaAC} has the largest amount of Na⁺ because of the introduction of Na⁺ in the mineralizer and although the acidified MIL-101-SO3H_{NaAc} possessed slightly less Na⁺, it was still higher than the other two samples. It is worth noting that the S content was also reduced after acidification, which results because the elemental S cannot be retained perfectly because much of the Na⁺ had fallen off. This result indicates that MIL-101-SO3HHCl has the maximum number of active groups.

3.1.4 XRD analysis. The obtained samples exhibited strong diffraction peaks (Fig. 3) at $2\theta = 2.77^{\circ}$, 3.30° , 5.10° , 8.40° and 9.00°, which corresponds to the crystal-plane diffraction of 311, 511, 531, 882 and 911, which are typical diffraction peaks for



Fig. 1 Nitrogen adsorption isotherms (A) and pore diameter distribution (B) of samples. (a) MIL-101-SO₃H_{HCL}, (b) MIL-101-SO₃H(Na)_{NaAC}, (c) MIL-101-SO3H_{HF}.

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Table 1 Nitrogen physical adsorption data of samples

Sample	$S_{ m BET}$ (m ² g ⁻¹)	$V_{\rm P}$ mesoporous (cm ³ g ⁻¹)	$V_{\rm P}$ micropore (cm ³ g ⁻¹)
MIL-101-SO ₃ H _{HCl}	1362	1.117	0.573
MIL-101-SO ₃ H _{NaAc}	1376	1.547	0.381
$\rm MIL\text{-}101\text{-}SO_3H_{\rm HF}$	1501	1.159	0.631



Fig. 2 FT-IR spectra of various catalysts. (a) MIL-101-SO $_3H_{HCL}$, (b) MIL-101-SO $_3H(Na)_{NaAC}$, (c) MIL-101-SO $_3H_{HF}$, (d) MIL-101.

MIL-101 (Cr).²³ This result indicates that the prepared MIL-101(Cr)-SO₃H has the same crystal-phase structure as the MIL-101(Cr), which correlates with the FT-IR characterizations. By comparison, the MIL-101(Cr)-SO₃H(Na)_{NaAC} and MIL-101(Cr)-SO₃H_{NaAC} samples have a similar crystal structure, but the MIL-101(Cr)-SO₃H_{NaAC} has a stronger diffraction peak at 2–6°. This results because Na⁺ is replaced by H⁺ through proton exchange,¹⁵ which yields neater crystal planes, after the acidification process.

3.1.5 Thermogravimetric analysis. The significant massloss stages of the three samples are shown in Fig. 4. The first mass-loss stage of the three samples at 30–125 °C, belongs mainly to the removal of water temperature from the samples. It is worth noting that the percent weightlessness of MIL-101- SO_3H_{HCl} is the least, that of MIL-101- SO_3H_{NaAC} is a little more and MIL-101- SO_3H_{HF} has the maximum percentage of weightlessness. Thus, MIL-101- SO_3H_{HCl} contains a minimum amount of adsorbed water. Then MIL-101- SO_3H_{HF} has a clear second-

Table 2The result of elemental analysis of chromium, sodium and Sfrom the different samples

Sample	S (wt%)	Cr (wt%)	Na (wt%)	Na ⁺ /S ³⁻
MIL 101 SO H	6 70	15 70	0.72	0.11
MIL-101-SO ₃ H _{HCl}	6.79	15.72	0.73	0.11
MIL-101-SO ₃ H(Na) _{NaAC}	7.10	13.88	2.65	0.37
MIL-101-SO3H _{NaAc}	6.05	13.8	2.04	0.34
MIL-101-SO ₃ H _{HF}	5.93	12.73	1.96	0.33



Fig. 3 XRD patterns of various catalysts. (a) MIL-101-SO₃H_{HCI}, (b) MIL-101-SO₃H_{(Na)NaAC}, (c) MIL-101-SO₃H_{HF}, (d) MIL-101-SO₃H_{NaAC}.

loss stage at 320–480 °C, because of the proportion of thermal decomposition of the –SO₃H group is much higher than that of the other two,²⁷ whereas MIL-101-SO₃H_{HCl} and MIL-101-SO₃-H_{NaAC} show a low mass loss. The third distinct mass-loss stage of MIL-101-SO₃H_{HCl} and MIL-101-SO₃H_{NaAC} occurred at 410–560 °C, and that of MIL-101-SO₃H_{HF} occurred at 480–660 °C, because the skeleton collapsed after the –SO₃H group decomposed slowly to generate hydride.³² Comparison of the weight loss of three samples, mass weightlessness of MIL-101-SO₃H_{HF} occurred first, after the removal of water, which indicates the thermal stability of MIL-101-SO₃H_{HF} is worst. And MIL-101-SO₃H_{HF} has the best stability than the other two.

3.1.6 NH₃-TPD analysis. To demonstrate the difference in acidity of the three samples, NH₃-TPD was used for characterization analysis (Fig. 5). To eliminate the signal effects that are caused by the high-temperature decomposition of samples, MIL-101-SO₃H(Na)_{NaAC} was processed in the temperature program without NH₃ adsorption. The peak plot of MIL-101-SO₃H(Na)_{NaAC} (does not adsorb NH₃) was divided into three peaks termed '1', '2', '3' (the peak area ratio is 1.0 : 2.0 : 2.6); these indicate the gradual decomposition performance of the catalyst, and proved the results of the thermogravimetric analysis. The NH₃-TPD peak diagram of MIL-101-SO₃H(Na)_{NaAC} was divided into five peaks (the peak area ratio is 0.3:1.0:1.5:2.0:2.6), the peak labeled '4' represents a weak acidity, and the peak labeled '5' manifests a medium-strong acidity. The five peaks of MIL-101-SO₃H_{NAAC} (the peak area ratio is 0.2 : 1.0 : 2.2 : 2.0 : 2.6) show that its medium-strong acidity



is stronger than that of MIL-101-SO₃H(Na)_{NaAC}, because more active components result from proton exchange of Na⁺ and H⁺. A weak and medium–strong acidity exist in the MIL-101-SO₃-H_{HCl} (the peak area ratio is 0.3 : 1.0 : 2.2 : 2.0 : 2.6) and MIL-101-SO₃H_{HF} (the peak area ratio is 0.2 : 1.0 : 1.4 : 2.0 : 2.6). For comparison, MIL-101-SO₃H_{HF} has the least amount of medium–strong acidity, and MIL-101-SO₃H_{HCl} has more proportion of weak acidity than MIL-101-SO₃H_{HCl} has more proportion of weak acidity than MIL-101-SO₃H_{HCl} is strongest in acidity and thermal stability.

3.1.7 XPS analysis. The elemental C, O, Cr, S and F in MIL-101-SO₃H are shown in Fig. 6A. A peak appears at 168 eV for S 2p, which indicates that all three samples contain sulfonic-acid groups. The split peak of S 2p with peak positions at 169.0 eV and 167.8 eV belongs to the peaks of R–SO₃H and R–SO₃R', respectively.³³ The ratio of peak distribution on the sample surfaces show that the proportion of MIL-101-SO₃H(Na)_{NaAC} (the peak area ratio is 1 : 1.62) is smallest, MIL-101-SO₃H_{HCl} (the peak area ratio is 1 : 1.58) is slightly smaller, and MIL-101-SO₃H_{HF} (the peak area ratio is 1 : 1.54) is largest. The Cr 2p has two peaks at 587.1 eV and 577.3 eV, respectively, which are typical Cr $2p_{1/2}$, Cr $2p_{3/2}$ split peaks,³⁴ and the peak distribution ratio of these three catalysts is not much different, whereas the proportion of MIL-101-SO₃H(Na)_{NaAC} (the peak area ratio is 1.8 : 1) is reduced slightly compared with that of MIL-101-SO₃-H_{HCl} (the peak area ratio is 1.9 : 1) and MIL-101-SO₃H_{HF}



Fig. 5 NH₃-TPD peak separation curve of four samples (a) MIL-101-SO₃H(Na)_{NaAC} (don't adsorb NH₃), (b) MIL-101-SO₃H(Na)_{NaAC}, (c) MIL-101-SO₃H_{NaAC}, (d) MIL-101-SO₃H_{HF}, (e) MIL-101-SO₃H_{HCI}.



Fig. 6 XPS spectra of various samples (A) survey spectrum. (a) MIL-101-SO₃H_{HCl}, (b) MIL-101-SO₃H(Na)_{NaAC}, (c) MIL-101-SO₃H_{HF}.



Fig. 7 SEM of three catalysts. (A) MIL-101-SO₃H_{HCL}, (B) MIL-101-SO₃H_{NaAC}, (C) MIL-101-SO₃H_{HF}.

(1.9:1). Moreover, the peaks of Na 1s in the three samples clearly prove that MIL-101-SO₃H(Na)_{NaAC} contains the maximum Na⁺, whereas MIL-101-SO₃H_{HCl} contains minimal

 Na^+ . Only MIL-101-SO₃H_{HF} has a small peak of F 1s at 164.2 eV, which indicates that F^- is involved in the construction of the framework in the synthesized catalyst.³⁵ However, the split

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Table 3	Results of catal	ytic performance	evaluation of	catalyst"

	Acid density	Cyclohexene	Cyclohexylformate selective (%)		
Sample	$(\text{mmol } g^{-1})$	conversion (%)		Literature	
MIL-101	_	5.30	67.15	This work	
MIL-101-SO ₃ H _{HCl}	0.82	63.97	97.61	This work	
MIL-101-SO ₃ H _{HF}	0.73	38.40	97.34	This work	
MIL-101-SO ₃ H _{NaAc}	0.76	32.46	97.71	This work	
SBA-15-SO ₃ H	0.23	54.40	95.80	19 and 20	
PSCSA ^b	0.81^{c}	87.80	97.40	10	
HZMS-5 ^b	1.70	77.60	97.00	12	
Nafion NR50 ^b	0.51	68.20	98.50	19	
Amberlyst-15	4.60	91.50	98.10	18	

^{*a*} Reaction conditions: cyclohexene = 4.11 g, n(cyclohexene) : n(HCOOH) = 1 : 3, m(catalyst) = 0.55 g, 80 °C, 6 h. Acid densities were calculated by elemental analysis and XPS. ^{*b*} Reaction was conducted into the autoclave at 413 K. ^{*c*} Based on S content by elemental analysis.





peaks of other elements show no clear difference. Therefore, with NaAC as a mineralizer, the introduction of a large amount of Na⁺ has a significant influence on the surface sulfonic-acid content in MIL-101-SO₃H, which results in a decrease in active groups on the catalyst surface.

3.1.8 SEM morphology. SEM analysis of the MIL-101-SO₃H prepared by three different mineralizers is shown in Fig. 7. The particle distribution of the three samples is uneven with obvious agglomeration.³⁶ MIL-101-SO₃H_{HCl} has the smallest particle size, whereas MIL-101-SO₃H_{HF} has the largest particle size, and MIL-101-SO₃H_{NaAC} shows little difference from MIL-101-SO₃H_{HF}, which is consistent with the literature.²⁷

3.2 Catalytic performance

The acidic concentration of the catalyst was calculated by elementary and XPS analysis. The results were listed in Table 3. It is clear that MIL-101-SO₃H_{HCl} has more acid content, and acid activities.

The conversion and selectivity of esterification catalyzed by obtained samples, shows that the MIL-101 exhibited almost no catalytic performance on esterification, and the cyclohexene conversion rate was only 5.30%. The catalytic performance of MIL-101-SO₃H_{HCl} was best, with cyclohexene conversion rate of 63.97%, and cyclohexyl formate selectivity of 97.61%. The catalytic performance of MIL-101-SO₃H_{HF}. So the $-SO_3H$ is the primary active group in MIL-101-SO₃H_{HF}. So the $-SO_3H$ is the primary active group in MIL-101-SO₃H and MIL-101-SO₃H_{HCl} performed best in this esterification. And after acidification of the MIL-101-SO₃H(Na)_{NAAC}, its catalyst reactivity increases to a certain extent.

Fig. 8 indicates the reusability of the three catalysts evaluated in this work. We can see that MIL-101-SO₃H_{HCl} can be recycled three times and the conversion rate of the esterification reaction remained at 37.6% with the selectivity of cyclohexyl formate keeping almost constant after the third run, whereas the fresh MIL-101-SO3H_{NaAC} can be only used for two runs and MIL-101-SO₃H_{HF} can keep run once only. The best performance of MIL-101-SO₃H_{HCl} is because of its maximum effective acid content and strongest tolerance compared with the other two, which are both key to determine the catalytic performance in this acid-catalyzed esterification. The poorest stability of MIL-101-SO3H_{HF} caused its worst productivity. Its fresh sample had started to collapse in the first time of esterification, so even though it has enough acid content, it did not generate the similar great result as MIL-101-SO3HHCI. And the performance of MIL-101-SO3H_{NaAC} occurred for the same reason. These results also correspond to previous thermogravimetric characterization analysis.

To establish the reason for the instability of MIL-101-SO₃H, the sample reusability was analyzed by fundamental characterization. The amount of adsorption of the three samples in the lower-pressure zone was reduced in the N_2 adsorption isotherms (Fig. 9A), which indicates that fewer catalyst micropores exist, mainly because the catalytic skeleton collapsed. This result is also suggested by the obvious displacement of the pore-size distribution of the three samples. The specific surface



Fig. 9 The N₂ isotherms and pore diameter distribution of three catalysts for three run times (A) (a) MIL-101-SO₃H_{HCL} (b) MIL-101-SO₃H_{NaAC}, (c) MIL-101-SO₃H_{HCL} and MIL-101-SO₃H_{HCL} with different run times (B), (d) fresh MIL-101-SO₃H_{HCL} (e) MIL-101-SO₃H_{HCL} run 1, (f) MIL-101-SO₃H_{HCL} run 3, (g) MIL-101-SO₃H_{HCL} run 5.



Fig. 10 XRD patterns of three catalysts for recovery in three run times and MIL-101-SO₃H_{HCl} with different run times (a) MIL-101-SO₃H_{HCl} fresh, (b) MIL-101-SO₃H_{HCl} run 1, (c) MIL-101-SO₃H_{HCl} run 3, (d) MIL-101-SO₃H_{HCl} run 5, (e) MIL-101-SO₃H_{NaAC}, (f) MIL-101-SO₃H_{HF}.

area of the MIL-101-SO₃H_{HCl} (877 m² g⁻¹) was retained after the first run time, but with an increase in run time, the catalyst structure began to change significantly until after the third run. The specific surface area of the fifth recovered catalyst is similarly small to that of the third run at 256 m² g⁻¹ and 124 m² g⁻¹, respectively (Fig. 9B), and the apparent change in pore-size distribution reveals that the catalyst collapsed until there were almost no micropores at the end. XRD patterns of the different MIL-101-SO₃H samples (Fig. 10) show that the crystallinity of the three catalysts after three runs is low. Although MIL-101-SO₃H_{HCl} still shows some distinct diffraction peaks, the diffraction peaks of the recovered catalysts are not as obvious as the diffraction peaks of the fresh catalyst, in accordance with the performance of the N₂ isotherms.

4. Conclusions

A comparison of MIL-101-SO₃H prepared by a one-pot synthesis using three different mineralizers to catalyze the esterification of cyclohexene with formic acid, highlighted the relatively better catalytic effect and stability of MIL-101-SO₃H prepared by HCl as a mineralizer. The catalytic action was retained up to three run times. However, the catalyst structure underwent significant changes as determined by XRD and N₂ adsorption characterization, because of the strong polarity of the reaction solution and the limited tolerance of the catalyst. Further work should be conducted to improve the acid amount of MIL-101-SO₃H and remain it better stability in a strongly polar system.

Conflicts of interest

There are no conflicts to declare.

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