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Synthesis of quinoline derivatives from anilines and aldehydes catalyzed by Cp_2ZrCl_2 and recyclable Cp_2ZrCl_2/MCM -41 system

Qiaoxia Guo*, Lijun Liao, Weiling Teng, Shenyong Ren, Xiao Wang, Yingying Lin, Fanfang Meng

State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum, 18# Fuxue Rd., Changping, Beijing 102249, China

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ABSTRACT

A facile method for the synthesis of quinoline derivatives using catalytic amount of Cp₂ZrCl₂ or Cp₂ZrCl₂ supported on MCM-41 (Cp₂ZrCl₂/MCM-41) in reaction of anilines and aldehydes is described. When Cp₂ZrCl₂/MCM-41 was used as catalyst, the yields of quinolines were enhanced by 5–15% compared with Cp₂ZrCl₂ as catalyst alone under the same reaction conditions. More importantly, Cp₂ZrCl₂/MCM-41 catalyst can be reused at least thrice by simple recover via filtration in air. Moreover, both Cp₂ZrCl₂ and Cp₂ZrCl₂/MCM-41 showed good catalytic activities to generate corresponding quinoline derivatives in moderate to good yields by varying the substituent of aniline and aldehyde. And the reaction conditions were optimized by studying the influences of reactant ratio, additives, solvent effect and reaction temperatures.

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1. Introduction

Quinolines have always been received great attention because of their broad chemical and biological activities. Five known methods are used to synthesize substituted guinoline derivatives including the Skraup reaction [1], the Doebner–von Miller reaction [2], the Conrad–Limpach reaction [3], the Friedländer reaction [4] and the Pfitzinger reaction [5]. The Doebner-von Miller reactions which are generally carried out in the presence of strong acid without any oxidants are particularly useful for large-scale synthesis of quinolines using simple substrate (anilines and aldehydes). Matsugi et al. [6] and Baba et al. [7] reported that quinoline could be synthesized in a two-phase solvent system which consists of an organic phase and an aqueous acid phase in order to avoid the tedious isolation procedure. In our previous work, we also found that yields of 2,3dialkylquinoline derivatives could be efficiently promoted by H₂O₂ in the presence of AlCl₃ at mild conditions without by-product formation [8]. Xi [9] and Ghorai [10] reported synthesis of variously substituted quinolines via transition-metal-free cyclization reaction. However, as all methods have several disadvantages such as special substrate, unfriendly strong acid or base, high temperatures

E-mail address: qxguo@cup.edu.cn (Q. Guo).

http://dx.doi.org/10.1016/j.cattod.2015.08.035 0920-5861/© 2015 Elsevier B.V. All rights reserved. or harsh conditions, tedious isolated procedure, waste production and no reusability which need to be overcome. Moreover, in terms of catalyst, various precious metals such as palladium, iridium, rhodium, ruthenium, lanthanum, bismuth, indium and gold nanoparticles have been used for the synthesis of quinoline derivatives [11–19]. Many of the catalysts are not fully satisfactory with regard to cost of catalysts, operational simplicity and catalyst stability. Therefore, to avoid these limitations, the exploration of new catalyst with good catalytic activity, reusability, simple work-up and isolated procedure for the synthesis of quinoline derivatives is highly required.

On the other hand, zirconocene dichloride (Cp₂ZrCl₂) catalyzed organic transformation and zirconium-mediated syntheses are widely used in organic chemistry. In the past years, Takahashi et al. [20] have reported 2,3-dihalopyridine such as 2-bromo-3-iodopyridine reacted with zirconacyclopentadienes to give 5,6,7,8-tetrasubstituted quinoline derivatives in good to high yields. In 2005, Wang reported nano-polyethylene fibers were prepared via in situ ethylene extrusion polymerization, with MCM-41 or SBA-15 supported zirconocene dichloride (Cp₂ZrCl₂) catalytic systems [21]. So far the applications of Cp₂ZrCl₂ have focused mainly on stereoselectivity of the reaction or syntheses of zirconium cation compounds and not on the construction of carbon–nitrogen bonds using aniline and aldehyde. Based on the high catalytic activity of Cp₂ZrCl₂ and the lower price than precious metals, we would like to report the synthesis of quinoline

^{*} Corresponding author at: China University of Petroleum, 18 Fuxue Road, Changping District, Beijing 102249, China.

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Scheme 1. Cp₂ZrCl₂-catalyzed reaction of aniline with *n*-butyraldehyde.

derivatives from aniline and aldehyde using Cp₂ZrCl₂ or Cp₂ZrCl₂ supported on MCM-41 (Cp₂ZrCl₂/MCM-41) as catalyst in this paper. It is worth noting that the latter catalyst has good catalytic activity, reusability and simple procedure.

2. Experimental

2.1. Materials

Zeolite Y, ZSM-5, H β and MCM-41 were synthesized in our laboratory according to the methods in the literatures [22–25]. Supported Cp₂ZrCl₂ catalysts used in this work were prepared by a conventional impregnation method. Typically, at room temperature, 3.75 mmol (1.095 g) Cp₂ZrCl₂ was dissolved in 20 mL tetrahydrofuran under gentle magnetic stirring. Next, the solution was dropped into 2.5 g MCM-41 and stirred for 24 h. Then the solution was dried in a conventional oven with air circulation at 75 °C for 24 h, after the impregnation pale yellow solids (Cp₂ZrCl₂/MCM-41) were obtained. THF was purified by distillation under nitrogen from sodium. Other starting materials were obtained from commercial supplies and used without further purification.

2.2. Characterization of the catalyst

Power X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 advance X-ray diffractometer. The texture property was determined by measuring the N₂ isotherm at -196 °C on a Micromeritics ASAP 2020 automated system. Elemental analysis was performed on a Rigaku ZSX 100e X-ray fluorescence (XRF) spectrometer. ¹H and ¹³C spectra were measured by JEOL JNM-ECA600.

2.3. Synthesis of quinoline derivatives

The first typical reaction was carried out with 1 mmol aniline and 4 mmol *n*-butyraldehyde added to the solution of 0.1 mmol Cp₂ZrCl₂ catalysts dissolved in 8 mL dichloromethane (DCM) in a dry Schlenk tube under nitrogen atmosphere at 40 °C. Dodecane was added as an internal standard. The mixture was stirred at 40 °C until the reaction was completed. The reaction mixture was then quenched with 3 M ammonia solution, and extracted with diethyl ether, then the combined organic layer was washed with water, brine, dried over sodium sulfate and concentrated to get a crude product, which was purified by column chromatography over silica gel using ether/petroleum ether (1/30) as eluent.

The second typical reaction was carried out with aniline (1.5 mmol), *n*-butyraldehyde (6 mmol), and Cp₂ZrCl₂/MCM-41 (0.1 g) in CH₂Cl₂ (12 mL). The mixture was stirred for 5 h at 40 °C in a dry Schlenk tube under nitrogen atmosphere. After cooling the reaction mixture, the catalyst was separated from the liquid product by filtration. It was concentrated and then purified by column chromatography over silica gel. The reaction was monitored by gas chromatograph to determine the yield of the product.

Catalytic activity was determined by the yield of quinoline derivatives using dodecane as an internal standard. The structures of the products were identified by ¹H, ¹³C NMR spectra and HRMS. The catalytic reaction was carried out with aniline (3 mmol), *n*-butyraldehyde (12 mmol), and Cp₂ZrCl₂/MCM-41 (0.2 g) in CH₂Cl₂ (24 mL). The mixture was stirred for 7 h at 40 °C under nitrogen atmosphere. After cooling the reaction mixture to room

temperature, the catalyst was separated from the liquid product by filtration. The recovered catalyst was washed with DCM, and dried at room temperature overnight under aerobic conditions, and then reused for the next reaction under the same conditions mentioned above.

3. Results and discussion

3.1. Synthesis of quinoline derivatives catalyzed by Cp₂ZrCl₂

When 1.5 mmol aniline reacted with 6 mmol *n*-butyraldehyde in the presence of 0.15 mmol Cp₂ZrCl₂ (0.1 equiv.) under nitrogen atmosphere, 3-ethyl-2-propylquinoline (**1a**) was obtained as a major product in 60% yield (Scheme 1). For the structure of 3ethyl-2-propylquinoline was determined by NMR spectrum shown in supporting information, no other isomer products could be isolated.

In addition, N-butylbenzenamine (**1b**) was obtained in 20% yield as a by-product. Considering the influence of temperature and solvents, we investigated this double carbon–nitrogen bond formation under various conditions. The optimal reaction conditions were 40 °C in DCM. Lower yields of **1a** were obtained, when the reaction temperature was decreased to 25 °C or raised to 50 °C. A broad number of solvents were tested for the reaction. Dichloromethane, toluene, acetonitrile, chloroform, dimethyl sulfoxide and 1,2-dichloroethane gave comparable yields of **1a** whereas lower yields were obtained with tetrahydrofuran.

In the further work, the amount of the reactants and the dosage of catalysts were varied. As shown in Table 1, an optimal aniline/aldehyde ratio of 1/4 is obtained. At lower ratios, the aldehyde tends to condense and product isolation becomes difficult. Also, we obtained good results when 0.1 equiv. of Cp₂ZrCl₂ was used. Treatment of 1 equiv. aniline and 4 equiv. *n*-butyraldehyde with 0.1 equiv. of Cp₂ZrCl₂ afford 60% quinoline and 20% N-butylaniline (entry 4). It shows essentially same yields compared to 1 equiv. of Cp₂ZrCl₂ as the catalyst (entry 7). This indicated that the overall transformation should be catalytic to Cp₂ZrCl₂. The reactions were also checked by using 0.05 equiv. catalyst, the yield of quinoline was 55% (entry 6), but the reaction time of 0.05 equiv. case was 32 h, as a result, 0.1 equiv. Cp₂ZrCl₂ was the best as the catalytic amount. In this reaction, firstly, the nucleophilic addition reaction of aniline with aldehyde occurs to give imine after elimination of

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D ₂ ZrCl ₂	catalyzed of	f aniline wi	th n-buty	raldehvde

Entry	Aniline: <i>n-</i> butyraldehyde: Cp ₂ ZrCl ₂	Conditions	Yield [%] ^b	
			Quinoline	N-Butylbenzenamine
1	1:1:0.1	40°C, 1 h	21	Trace
2	1:2:0.1	40°C, 18 h	53	14
3	1:3:0.1	40°C, 7h	47	20
4	1:4:0.1	40°C, 5h	60	20
5	1:5:0.1	40 °C, 8 h	59	27
6	1:4:0.05	40°C, 32 h	55	19
7	1:4:1	40°C, 4h	63	37

^a 12 mL DCM was used as solvent.

^b The yields are relative to aniline and were determined by gas chromatography with dodecane as an internal standard.

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a H₂O. Then, the addition of another molecule of aldehyde (enol tautomer of aldehyde) to imine to form 1-hydro-2,3-disubstituted quinolin-4-ol, followed by dehydration and dehydrogenation to afford quinoline derivatives, at the same time imine can be easily reduced by this two hydrogen to form *N*-alkylaniline probably according to our previous proposed mechanism [8].

Generally the yield of quinoline derivatives from the reaction of aniline and aldehyde is not quantitative since the by-product of N-alkylbenzenamine was in situ formed by addition of H (generated from H elimination of dihydroquinoline) on imine, but this procedure provides a convenient and facile synthesis method of a series of quinolines with varied substituents such as Cl, Br, Me, OMe. However, this reaction still has some drawbacks such as tedious work-up leading to the generation of large amount of toxic waste and the catalysts are destroyed which cannot be reused or recovered. So we investigated this reaction over supported catalysts to overcome these drawbacks.

3.2. Synthesis of quinoline derivatives over porous materials

In 1997, a US Patent reported the synthesis of quinolines by vapor phase reaction of aniline base and aliphatic aldehyde at $350 \,^{\circ}$ C over solid acid catalysts [26]. These catalysts are porous materials include ZSM-5, zeolite- β and zeolite-Y which could provide either Br ϕ nsted or Lewis acidity. This method provides a convenient process for the preparing of quinolines with low yields. So there still remains a need for the improved synthesis of quinolines which include clean and efficient technology.

Firstly, we investigated the synthesis of quinolines mediated by different porous materials. All reactions were performed at 40 °C for 24 h in CH₂Cl₂ without Cp₂ZrCl₂. The results were shown in Table 2. The catalyst including, for example zeolite- β and zeolite-Y, showed certain catalytic activity in the absence of Cp₂ZrCl₂ (Table 2, entries 2–4). However, ZSM-5 is not effective for the synthesis of quinoline (Table 2, entry 5), the reason might be its pore diameter is too small and it prevents the formation of the relatively large molecules of quinoline derivatives.

Then the effects of different additives for the synthesis of quinoline derivatives catalyzed by Cp₂ZrCl₂ were examined as shown in Table 3. Six kinds of porous materials are used as additives in this reaction. High catalytic activity was observed when MCM-41 or HY was added in the reaction of aniline and *n*-butyraldehyde catalyzed by Cp₂ZrCl₂ (Table 3, entries 3 and 7). The high activity of HY is attributed to its higher acidity and the high activity of MCM-41 is attributed to its large pore size as well as large surface area of it, which leading to a higher dispersion of Cp₂ZrCl₂. Silica gel, USY and ZSM-5 were less effective for this reaction with yields of 39%, 17% and 40% (Table 3, entries 1, 2 and 5), respectively. ETS-10 (a microporous titanosilicate with a three-dimensional 12ring pore system) almost showed great prohibitive effect with only trace amount of quinoline produced (Table 3, entry 6). Reaction with zeolite- β showed moderate conversion with a yield of 56%

Table 2

Study on the synthesis of quinoline catalyzed by different porous materials.^a

Entry	Mediator	Yield [%] ^b	
		Quinoline	N-Butyl-aniline
1	Silica gel	10	Trace
2	USY	15	Trace
3	HY	25	Trace
4	Нβ	33	Trace
5	ZSM-5	Trace	Trace
6	MCM-41	15	Trace

 $^a\,$ Aniline (1 mmol), butyraldehyde (4 mmol), mediator (0.1 g) in CH_2Cl_2 40 °C. $^b\,$ GC yields based on aniline.

Га	b	le	3	

Effects of different additives on the synthesis of quinoline catalyzed by Cp₂ZrCl₂.^a

Entry	Additive	Yield [%] ^b	
		Quinoline	N-Butyl-aniline
1	Silica gel	39	Trace
2	USY	17	Trace
3	HY	68	27
4	нβ	56	Trace
5	ZSM-5	40	Trace
6	ETS-10	Trace	Trace
7	MCM-41	81	14
8	-	60	20

 $^a\,$ Aniline (1 mmol), butyraldehyde (4 mmol), Cp_2ZrCl_2 (0.1 mmol), additive (0.1 g) in CH_2Cl_2 40 $^\circ C.$

^b GC yields based on aniline.



Fig. 1. Powder XRD patterns of MCM-41 and Cp₂ZrCl₂/MCM-41.

(Table 3, entry 4). Results of Tables 2 and 3 show that MCM-41 is the most suitable and efficient carrier for this Doebner–von Miller reaction catalyzed by Cp_2ZrCl_2 .

3.3. Characterization of Cp₂ZrCl₂/MCM-41

Cp₂ZrCl₂/MCM-41 was prepared as mentioned in experimental Section 2.1. Fig. 1 shows powder XRD patterns of MCM-41(A) and Cp₂ZrCl₂/MCM-41(B). The peaks corresponding to MCM-41 was observed in the low-angle region, however the slight decrease in peak intensities was observed after impregnation of Cp₂ZrCl₂ onto MCM-41, the possible reason for the decreases in XRD peak intensity of Cp₂ZrCl₂/MCM-41 may attribute to the adsorption effect to the X-ray by Cp₂ZrCl₂ layer on the inner or outside surface of MCM-41. The amount of Cp₂ZrCl₂ in Cp₂ZrCl₂/MCM-41 is calculated in 1.37 mmol/g based on the results of XRF analysis. A slightly decrease of surface area which was obtained by nitrogen physisorption of Cp₂ZrCl₂/MCM-41 was also observed. The XRD patterns and nitrogen physisorption data of Cp₂ZrCl₂/MCM-41 obviously indicate that the mesoporous array structure was not destroyed during the modification with Cp₂ZrCl₂.

3.4. Synthesis of quinoline derivatives catalyzed by Cp₂ZrCl₂/MCM-41

Table 4 shows the influence of temperature and solvents and the comparison of the results of aniline reacted with *n*-butyraldehyde catalyzed by Cp_2ZrCl_2 and $Cp_2ZrCl_2/MCM-41$. Catalytic activity

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Table 4	
Comparison of the results of synthesis of quinoline catalyzed by	/ different catalysts

Entry	Catalyst	Temperature/°C	Solvent	Yield [%] ^b	
				Quinoline	N-Butylbenzenamine
1	Cp ₂ ZrCl ₂	25	DCM	37	14
2	Cp_2ZrCl_2	40	DCM	60	20
3	Cp_2ZrCl_2	40	DCE	49	15
4	Cp_2ZrCl_2	50	DCE	56	15
5	Cp ₂ ZrCl ₂ /MCM-41	25	DCM	50	Trace
6	Cp ₂ ZrCl ₂ /MCM-41	40	DCM	65	18
7	Cp ₂ ZrCl ₂ /MCM-41	50	DCE	58	19

^a Aniline (1 mmol) and butyraldehyde (4 mmol) were used.

^b GC yields based on aniline.

decreased with decreasing reaction temperature: only small amount of quinoline (yield of 37%) was detected during the reaction (entries 1 and 5) at 25 °C. However, the catalytic activity was enhanced by elevating the reaction temperature. But a temperature of 50 °C does not show any obvious improvement compared to the yield at 40 °C (entries 3, 4, 6, and 7). According to these results, a temperature of 40 °C is deemed suitable for the reaction. Reactions in dichloromethane showed good catalytic activity with yields of 60% and 65%, respectively (entries 2 and 6). Dichloroethane (DCE) was less effective with 56% and 58%, respectively (entries 4 and 7). From these results, we chose dichloromethane as a suitable solvent for further research. Finally, results in Table 4 indicate that reactions of Cp₂ZrCl₂/MCM-41 showed a little bit higher catalytic activity than that of Cp₂ZrCl₂. However, it is somehow lower than the MCM-41 as additive case (Table 3, entry 7). This may be due to the deposition of Cp_2ZrCl_2 in the pore surface of MCM-41 during the impregnation which results the decrease of the activity of Cp₂ZrCl₂/MCM-41. Whereas the reaction mixture of Cp₂ZrCl₂/MCM-41 does not need the ammonia solution quenching and solvent extraction procedures, which would makes the process of the reaction much facile and environmentally friendly.

We are interested in the scope and limitations of various anilines and aldehydes. The results are summarized in Table 5. In general, the yields of quinoline were affected obviously by the nature of substituents on aniline. Anilines have an electron-donating group such as *p*-toluidine, 4-methoxybenzenamine, o-toluidine and 2methoxybenzenamine gave corresponding products in good yields, although small amount of secondary amines were accompanied as a by-product (Table 5, entries 1, 2, 6, and 7). The secondary amines formation was due to the intermediate imine during the reaction. On the other hand, reactions of 4-nitrobenzenamine having an electron-withdrawing group give 3-ethyl-6-nitro-2propylquinoline in low yield (Table 5, entry 5). This may be due to the nucleophilic ability of amino- group (-NH₂) was decreased by nitro group $(-NO_2)$ leading to nucleophilic addition reaction of aniline and aldehyde unresponsive. A higher yield of the reaction of aniline and octylaldehyde was obtained by using Cp₂ZrCl₂/MCM-41 in toluene at 100 °C (Table 5, entry 11). However, we do not observe quinoline derivatives using aniline and cinnamaldehyde (Table 5, entry 12). This may be due to the stability of cinnamaldehyde which could not tautomerize to enol format for further cyclization to form tetrahydroquinoline. It is consistent with the mechanism that we speculated previously about synthesis of quinoline [8]. Interestingly, the reactions of 4-chlorobenzenamine or 4bromobenzenamine with aldehyde showed good yields. Moreover, when Cp₂ZrCl₂ was supported on MCM-41 (Cp₂ZrCl₂/MCM-41) and used as catalyst, the yields of quinolines were enhanced by 5-15% compared with Cp₂ZrCl₂ as catalyst alone under the same reaction conditions.

3.5. The reuse of Cp₂ZrCl₂/MCM-41

We also investigated the reuse of catalyst in the reaction of aniline with *n*-butyraldehyde. The catalyst was simply recovered by

Table 5

Effects of different anilines and aldehydes on synthesis of quinoline derivatives.^a

R_1	+ R_2CH_2CHO NH ₂	$\xrightarrow{\text{cat.}} R_1 \xrightarrow{ }$	R_2 + R CH ₂ R ₂	NHCH ₂ CH ₂ R ₂		
Entry	Aniline	Aldehyde	Yield [%] ^b			
			Quiline		N-Butylbenzen	amine
			Cp ₂ ZrCl ₂	Cp ₂ ZrCl ₂ /MCM-41	Cp ₂ ZrCl ₂	Cp ₂ ZrCl ₂ /MCM-41
1	p-CH₃	CH ₃ CH ₂ —	66(60)	81	22	16
2	p-OCH ₃	CH ₃ CH ₂ —	76(62)	79	13	11
3	p-Cl	CH ₃ CH ₂ —	60(52)	72	12	Trace
4	p-Br	CH ₃ CH ₂ —	62(59)	71	Trace	Trace
5	p-NO ₂	CH ₃ CH ₂ —	24(20)	29	Trace	Trace
6	o-CH ₃	CH ₃ CH ₂ —	62(58)	68	Trace	Trace
7	o-OCH ₃	CH ₃ CH ₂ —	75(70)	79	9	9
8	m-CH ₃	CH ₃ CH ₂ —	60(58)	69	15%	17
9	Н	CH ₃ CH ₂ —	60(51)	65	20%	18
10	Н	$CH_3(CH_2)_5$	50(39)	54	Trace	Trace
11	Н	$CH_3(CH_2)_5$. /	72		Trace
12	Н	Ph-CH=CHCHOd		-		-

 $^a~$ Aniline (1 mmol), butyraldehyde (4 mmol), in CH_2Cl_2 at 40 $^\circ C.$

^b GC yields, isolated yields are in parentheses.

 $^{\rm c}~$ Aniline (1 mmol), octyl aldehyde (4 mmol) in methylbenzene at 100 $^{\circ}\text{C}.$

^d When aniline reacted with cinnamaldehyde, only N-(3-phenylallylidene)benzenamine (Ph—N=CH—CH—CH—Ph) was obtained quantitatively.

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Table 6

Specific surface area (S_{BET}), total pore volume (V_T) and average pore diameters (D_a) of the used catalysts (Cp₂ZrCl₂/MCM-41).

Entry	Number of cycles	$S_{\rm BET}~(m^2/g)$	$V_{\rm T}~({\rm cm^3/g})$	$D_{\rm a}({\rm nm})$
1	1st	700	0.54	3.06
2	2nd	697	0.56	3.23
3	3rd	699	0.55	3.13
4	4th	730	0.63	3.42
5	5th	811	0.73	3.61

Table 7

Reusability of Cp₂ZrCl₂/MCM-41 in the reaction of aniline and *n*-butyraldehyde.^a

Entry	Number of cycles	Zr (mmol/g) ^b	Yield [%] ^c	
			3-Ethyl-2- propylquinoline	N-Butylbenzenamine
1	1st	2.05	65	18
2	2nd	1.99	58	Trace
3	3rd	1.89	42	Trace
4	4th	1.84	25	Trace
5	5th	1.78	10	Trace

 a Aniline (1 mmol), butyraldehyde (4 mmol), Cp_2ZrCl_2/MCM-41 (0.1 mmol/0.05 g) in CH_2Cl_2 at 40 $^\circ C.$

^b The amount of Zr on the used catalyst analyzed by XRF.

^c GC yields based on aniline.

filtration and reused after washing with dichloromethane and drying at room temperature. All recycling procedures were carried out under air condition without any special air manipulation and the properties of these used catalysts are listed in Table 6. The specific surface area (S_{BET}), total pore volume (V_T) and pore diameters (D_a) of Cp₂ZrCl₂/MCM-41 increased generally with the increasing number of use.

To investigate the reusability of the catalyst, a Cp₂ZrCl₂/MCM-41 sample, in which the Zr concentration is 2.0 mmol for each gram of MCM-41, was prepared for the reaction of aniline and butyraldehyde. The yield of 3-ethyl-2-propylquinoline was gradually decreased from 65% in the first run to 10% in the fifth recycle as shown in Table 7. XRF analyses of used catalyst obviously indicated leaching of Cp₂ZrCl₂ during the recycling from 2.05 to 1.78 mmol/g of Zr (Table 7, column 3). Fig. 2 shows XRD patterns of used catalysts. The peak intensities also increased with the increasing number of cycles. This is in accordance with the increase in S_{BET}, V_T and D_a data of Cp₂ZrCl₂/MCM-41 increased generally with the increasing



Fig. 2. Powder XRD patterns of used catalysts.

number of recycling. These results clearly show that the loss of the catalyst indeed happened during recycling. According to the results, Cp₂ZrCl₂/MCM-41 could be reused at least three times with slightly decreasing the yield and the catalysts are air stable during the reaction and recycling.

4. Conclusions

In summary, the reaction that described in this paper provided a new application of Cp₂ZrCl₂ and Cp₂ZrCl₂/MCM-41 which were used as the catalysts to synthesize quinoline derivatives. This procedure is efficient and convenient. The addition of HY or MCM-41 effectively promoted the reaction catalyzed by Cp₂ZrCl₂. Cp₂ZrCl₂ supported on MCM-41 (Cp₂ZrCl₂/MCM-41) showed good activity in the synthesis of quinoline derivatives. Moreover, Cp₂ZrCl₂/MCM-41 could be reused at least thrice with moderate to good activity in the reaction. Reactions of various anilines with aldehydes gave good yields of the corresponding products, and the reaction conditions were optimized by studying the influences of reactant ratio, additives, solvent effect and reaction temperatures. The Nbutylbenzenamine formation was observed in this reaction as a by-product.

Supplementary material

The ¹H, ¹³C NMR, the HRMS data, as well as the NMR spectra of the quinoline derivatives synthesized, the TEM images and IR spectra of MCM-41 and Cp₂ZrCl₂/MCM-41 in this work can be found in the Supplementary Information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.08.035.

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