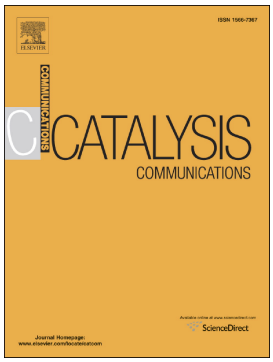

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High efficiency microwave-assisted synthesis of quinoline from acrolein diethyl acetal and aniline utilizing Ni/Beta catalyst

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ABSTRACT

A facile and solvent-free microwave-assisted approach to quinoline was developed by utilizing both acrolein diethyl acetal and aniline as reagents, firstly employing Ni/Beta zeolite as mild, ecofriendly and low-cost solid catalyst. As high as 83% yield of quinoline was quickly achieved at a short microwave time. The results indicated that the effect of Ni on Beta zeolite not only significantly promoted conversion of acrolein diethyl acetal to effective intermediate but also dramatically accelerated dehydrogenation rate of tetrahydroquinoline/dihydroquinoline to quinoline.

Keywords: microwave-assisted, acrolein diethyl acetal, quinolines, Beta zeolite

1. Introduction

Quinolines(Quinoline and its derivatives), as an important class of nitrogen heterocyclic compounds, have extensive application prospects in various fields. In particular, quinoline can act as a building block for the preparation of a wide range of value-added products applied in many industries such as pharmaceuticals, fungicides, herbicides, corrosion inhibitors and functional chemicals.[1-6] The typical quinolines synthesis methods involved Skraup[7, 8], Friedlander[9, 10], Doebner-Miller[11, 12], Conrad-Limpach[13, 14] and other methods[15-17], which could be carried out via conventional liquid-phase, vapor-phase or microwave route. Among these routes, compared with conventional thermal conditions requiring long reaction time and poisonous organic solvent, the microwave-assisted route is straightforward, quickly, solvent-free and heating evenly, which play more and more important role in quinolines synthetic strategy.

Up to now, there are many literature reports relating to microwave-assisted synthesis of quinoline derivatives, but most of them employed various unsaturated aldehydes/ketones or alkynes as one of reagent, such as alkyl vinyl ketones[18, 19], crotonaldehyde[20], cinnamaldehyde[21] and phenylacetylene[22]. Unfortunately, unsaturated aldehydes/ketones and alkynes as reagent were toxic, expensive and prone to polymerization during reaction, which is difficult to fulfill strict

requirements for environmental protection at present and then distinctly restricts the further development of quinolines synthesis. acrolein diethyl acetal(ADA), as a valuable chemical compound, possesses extraordinary diffusion ability and chemical stability, which is usually used to protect carbonyl group and also significantly avoids acrolein's relatively high cost and propensity to oligomerize when acrolein was directly used as reagent.[23, 24] Moreover, the procedure for the preparation of acetal is straightforward, which could be directly produced by corresponding aldehydes/ketones with alcohols with high conversion as well as excellent selectivity[23, 25]. Recently, Bryan J. Cowen reported that the reaction of ADA and aniline could obtain quinoline with high yield[26]; the only drawback is the reaction time up to 24 h under traditional thermal condition. Anyway, ADA shows a very promising future in quinolines synthetic reactions.

In the microwave-assisted synthetic quinolines routes, sulfuric acid, K10, $InCl_3/SiO_2$, phosphotungstic acid, $AgOTf/NH_4PF_6$, CuCl/Mont, functionalized-ionic liquid were usually employed as catalyst[18-22], which existed low selectivity, expensive or not environment-friendly at present. On the contrary, metal-modified zeolite possess large surface area, excellent hydrothermal stability as well as flexible adjustable active sites, which was utilized as catalyst to synthesize quinolines and exhibited excellent catalytic performance previously in conventional

liquid- or vapor-phase synthetic routes[27, 28]. Hence, in the presence work, a facile, fast and solvent-free microwave-assisted approach to quinoline utilizing ADA as one of reagent was provided, firstly employing metal-loaded zeolite as mild, ecofriendly and low-cost solid catalyst. High yield of quinoline was achieved over Ni/Beta catalyst undergo short microwave reaction time.

2. Experimental

2.1. Catalysts preparation

The Beta, ZSM-5, and Y zeolites were supplied by Nankai University Catalyst Factory; and all the chemicals were commercially available and had analytic purity. The metal-modified Beta catalysts were prepared by deposition-precipitation method. The typical procedures were as follows: The Beta zeolite powder was first added into the mixture aqueous solution containing a calculated amount of 0.2 M $Ni(NO_3)_2$ and excessive urea. The suspension was strongly stirred at room temperature for 1 h and then heated to 90 ℃ to refluxing for 4 h. subsequently, the resultant was cooled to room temperature, filtrated and washed with deionized water. Finally, the obtained solid was dried at 120 °C for 12 h and calcined at 550 °C for 4 h. The thus-prepared catalysts were denoted as Ni/Beta. The similar preparation method for other metal (metal: Zn, Fe, Cu and Mn) oxides supported catalysts.

2.2. Catalytic performance evaluation

General procedure for synthesis of quinolines from anilines and ADA was carried out in Panasonic NN-K5541JF microwave oven reactor equipping a magnetic stirring device. The typical procedures were as follows: ADA (1 mmol), excessive anilines (4 mmol) and solid catalyst were charged into a round-bottom flask; and then, the mixtures was placed into microwave reactor. The reaction was conducted by continuous microwave irradiation for 1-40 min under refluxing and stirring condition. Finally, the resulting products were determined by GC-MS of Varian Saturn 2200/ CP-3800 gas chromatography–mass spectrometry equipped with two CP8944 capillary columns (VF-5, 30 m × 0.25 mm × 0.25 μm).

2.3. Catalysts Characterization

X-ray diffraction spectroscopy was performed with a Bruker D8-Advance X-ray diffractometer. The detection conditions as follow: Cu target *Kα* ray (λ=1.54187 Å); scanning voltage 40 kV, scanning current 40 mA; scanning speed 0.2 s, scanning step 0.02°. N_2-physisorption was conducted on a Quantachrome Autosorb-1 instrument. Firstly, the catalyst was in situ outgassed at 300 °C for 12 h under a vacuum of 10^{-8} Torr. Subsequently, the specific surface area was calculated by multipoint BET equation, and the total pore volume was calculated at relative pressure of P/P_0=0.99. Temperature programmed desorption of NH_3 was determined on a Micromeritics Autochem II 2920 instrument. Firstly, the catalyst was pretreated at 400 °C for 30 min in a

flow of helium (99.99%) with a flow rate of 60ml/min and then cooled to 100 °C. Ammonia was pulse-injected in a stream of 10 % NH_3/He to achieve saturation adsorption of catalyst. After purging with helium at 100 °C for 1.0 h, ammonia was desorbed by heated the catalyst from 100 °C to 800 °C at a rate of 10 °C/min.

3. Results and discussion

3.1. Catalysts performances

Table 1 shows catalytic performances of various catalysts for microwave-assisted synthesis of quinoline from ADA and aniline. When various parent zeolites are used as catalysts respectively, the yield of quinoline is extremely low with low conversion of ADA. The completion of this reaction is considered to undergo two steps, containing decomposition of ADA to acrolein and/or other intermediate and subsequent condensation with aniline to quinoline, as shown in Eqs. (1).

$$CH_2{=}CH\text{-}CH(OEt)_2 \xrightarrow[\textbf{MW/Cat.}]{} CH_2{=}CH\text{-}CHO \ \textit{or}\ \text{other intermediate} \xrightarrow[\textbf{MW/Cat.}]{\text{Ph-}NH_2} \text{quinoline} \quad (1)$$

Thus, the terrible catalytic activity of pure zeolites is probably due to the low decomposition of ADA to effective intermediate. When various metal-loaded Beta zeolites are used as catalyst, respectively, both conversion of ADA and yield of quinoline increase sharply; and particularly as high as 83.1% yield of quinoline with complete conversion of ADA is achieved over Ni/Beta catalyst. The result indicates that the addition of metal on Beta zeolite catalyst significantly promote

decomposition of ADA to effective intermediate and subsequently condensation with aniline to form target product. Furthermore, when moderate water is added into reaction system, the yield of quinoline slightly decreases instead. Besides, the amount of catalyst also affects the conversion of ADA as well as yield of quinoline, as shown in Fig. S1. With increasing amount of catalyst, both conversion of ADA and yield of quinoline firstly increase obviously and subsequent decrease slightly,. This result is probably due that, more active sites could be provided to complete this reaction with appropriate increasing amount of catalyst, however, excessive active sites may be induce some side reactions, such as alkylation of quinoline, deep decompose of ADA and et. al, which decrease the yield of quinoline.

Fig.1 shows the effect of microwave time for quinoline yield over Beta and Ni/Beta catalysts. with increasing microwave irradiation time, the yield of quinoline just reaches to 32.1% after 40 min over the Beta catalyst, while that of quinoline sharply increases to 83.1% after 5 min over the Ni/Beta catalyst. The results show that, relative to the Beta catalyst, the Ni/Beta one is capable to accomplish much higher yield of quinoline under extremely short microwave time. This occurs probably due to the fact that the Ni-loaded on Beta zeolite accelerates the decomposition of ADA to effective intermediate and promotes the formation of quinoline subsequently under microwave reaction condition.

Therefore, the Ni/Beta catalyst exhibits high-effective catalytic performance. What is more, the Ni/Beta catalyst possesses a good recyclable performance, and its catalytic activity is near same to the fresh one after reusing four times under microwave and free-solvent condition, as shown in Fig. S2.

Fig.2 shows the effect of reaction time for product distribution over Beta(**I**) and Ni/Beta(**II**) catalyst. By means of mass spectrometric detection for product mixtures, it confirms that, besides quinoline, dihydroquinoline (2HQ) and tetrahydroquinoline (4HQ) are also generated during the reaction, as shows in Fig. S3. Over the Beta catalyst, high yield of 2HQ and 4HQ, which even exceeds that of quinoline, are obtained with 5 min microwave reaction; and meanwhile, the yield of 4HQ increases in entire reaction process while that of 2HQ increases firstly and decreases generally subsequently with increasing microwave time. Finally, the total yield of 4HQ and 2HQ still reaches to 23% after 40 min microwave irradiation. the result indicates that, with increasing microwave irradiation time, ADA is cracked and further condensed with aniline to form more 4HQ; and meanwhile, certain 2HQ is dehydrogenized to quinoline especially during 10-20 min reaction time. Besides, it is noteworthy that the level of side reactions also increase with prolonging reaction time over the Beta catalyst. Over the Ni/Beta catalyst, the total yield of 4HQ and 2HQ is 22% with 1 min microwave reaction

time, while that of 4HQ and 2HQ significantly decreases to 3.5% after only 5 min microwave reaction time; and meanwhile, the conversion of ADA is much higher than that over the Beta catalyst. The results indicate that, relative to the Beta catalyst, the Ni/Beta catalyst not only significantly accelerates the conversion of ADA but also effectively promote the process of dehydrogenation of 4HQ and 2HQ to quinoline.

Table 2. shows the reaction of ADA with various substituted anilines over Ni/Beta catalyst. Such as, o-, m- or p-methylaniline reacts with ADA to deliver 8-, 7- or 6-methylquinoline in 58.4%, 41.3% and 66.8% yield, respectively. Weak results are obtained with m- or o-nitroaniline reacting with ADA to deliver target quinolines products with just 25.8% and 19.4% yield, and the reaction of 2-hydroxyaniline and ADA delivers 31.3% yield of 7-hydroxyquinoline. Besides, o- and p-methoxyaniline reacts with ADA can obtain 65.3% and 57.2% yield of corresponding substitute quinoline, respectively; while the reaction of o-/p-chloroaniline and ADA delivers 8-/6-chloroquinoline in only 32.1% and 27.9% yield. It is noteworthy that, relative to aniline, other various substituted anilines reacting with ADA result in the decreased yield of desired quinolines, to different extent; and particularly, the yield of quinolines decreases more obviously using substituted aniline with electrondrawing group as reagent. This occurs probably due to the negative effects of stereo-hindrance of substituent group on benzene ring and/or the restraint of the condensation

of substitute anilines and intermediate because of the existence of electrondrawing group.

the reactions of other reagent and aniline to form desired quinolines also were investigated, as shown in table 1S. Glycerol and acetaldehyde as reagent respectively reacting with aniline can not generated quinoline or methylquinoline, probably due to the difficulty of glycerol dehydrating to intermediate acrolein or the leaving of acetaldehyde from reaction system rapidly because of its high volatility under microwave environment. Furthermore, acrolein directly as reagent reacting with aniline indeed synthesizes quinoline, but the yield of quinoline is very low (31.6 %) with full conversion of acrolein, which may arise from acrolein side reactions and/or fast volatility from reaction system. Relative to acrolein, ADA not only retains high chemical activity of olefinic bond but also protects its carbonyl group via acetalization which could restrain the level of side reactions effectively. Therefore, among various raw materials, ADA as the optimized reagent reacting with aniline can achieve high yield of quinoline.

3.2. Catalysts characterization

The Beta, Ni/Beta and reused-Ni/Beta catalysts are characterized by XRD, BET and NH_3-TPD methods. XRD patterns for catalysts are shown in Fig. 4S. All the catalysts show the characteristic of Beta zeolite and contain no diffraction peaks of Ni species for Ni/Beta catalysts, indicating

that Ni species are highly dispersed on Beta zeolite. Besides, the reused-Ni/Beta catalyst have almost same diffraction intensities relative to the fresh one, implying that the structure of Ni/Beta is considerably stable under microwave condition.

N_2-adsorption/desorption isotherm are shown in Fig. 5S. The isotherms of All the catalyst rise steeply at extremely low relative pressure and exist a weak hysteresis loop at $P/P_0 > 0.4$, indicating the existence of microporous and some mesoporous probably deriving from Beta secondary particle piled pore. The detailed textural properties of catalysts are also listed in table 2S. the Ni/Beta catalyst has the smaller surface area (S_{BET}, S_{ext}, S_{mic}), pore volume (V_{total}, V_{mic}) as well as micropore size (D_{mic}) than the pure Beta one. The decreased microporosity of Ni/Beta is mainly due to certain occupation in micropores by Ni component. Especially, the reused-Ni/Beta catalyst shows little decrement of S_{BET}, S_{ext}, S_{mic} and V_{total}, further indicating the good stability of Ni/Beta catalyst after recycling.

The acidity property of catalyst are shown in Fig 6S. All the catalyst exist T_1 peak, attributing to weak acid sites.[29, 30] The T_2 peak is identified obviously over the Beta catalyst but virtually absent over the Ni/Beta one, assigning to strong Brønsted acid sites. The T_3 peak appearing distinctly over Ni/Beta catalyst is attributed to strong Lewis acid sites deriving from Ni-supported on Beta zeolite with certain

interactions. The detail acidity date shows that, as listed in table 3S, the Beta catalyst possesses a larger strong Brønsted acid sties while the Ni/Beta one presents more strong Lewis acid sites; and especially, concentration of both weak acid and strong Lewis acid over Ni/Beta catalyst decreases little even if reuse four times. Therefore, combining with catalyst performance, it is concluded that the introduction of Lewis acid into Beta zeolite is favorable to generation of quinoline under microwave condition.

3.3. Reaction pathways

Hence, a plausible reaction mechanisms from aniline and ADA under microwave condition is speculated. ADA firstly converts to the protonated acrolein and/or oxocarbenium ion[26], and then reacts with aniline to generate unsaturated imine. Subsequently, imine reacts with another aniline to form double-benzene-structured imine, which converts to 4HQ via hydrogenolysis. Finally, the 4HQ transforms to 2HQ and further delivers to quinoline via dehydrogenation. Besides, the generated-protonated acrolein and/or oxocarbenium ion could react with aniline to form aniline propanal via michael addition, and subsequent generate quinoline via the process of cyclization, dehydration and dehydrogenation. Still, the mechanism relating to synthesis of quinoline form ADA and aniline under microwave condition (especially the formation of 4HQ) in the present case is not fully understood, which need

to be further investigated.

4. conclusion

A fast, facile and solvent-free microwave-assisted approach to quinoline with ADA as one of reagents was provided, in which high yield of quinoline was obtained utilizing Ni/Beta as mild, ecofriendly and low-cost solid catalyst. The addition of Ni on catalyst not only significantly promoted the conversion of ADA to effective intermediate but also dramatically accelerated the dehydrogenation rate of tetrahydroquinoline/dihydroquinoline to quinoline. Moreover, a series of substituted quinolines are obtained, using various substituted anilines reacting with ADA over Ni/Beta catalyst under microwave irradiation.

Acknowledgments

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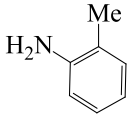
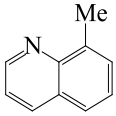
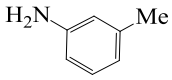
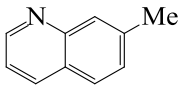
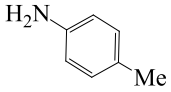
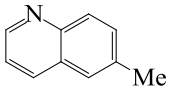
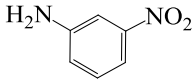
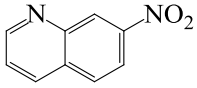
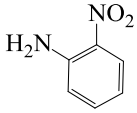
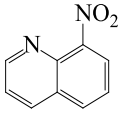
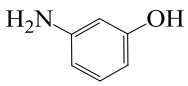
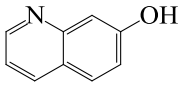
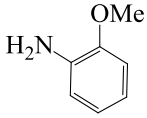
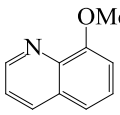
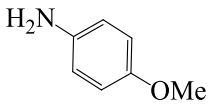
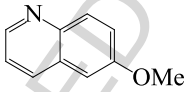
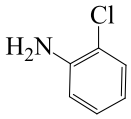
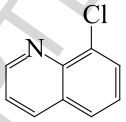
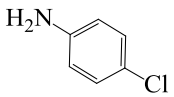
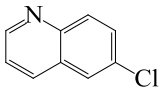
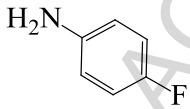
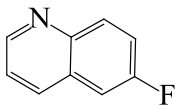
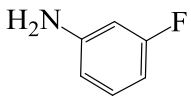
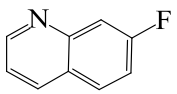
Table captions

Table 1 Catalyst performance over various zeolite-base catalysts

Catalyst	ADA:Cat:H_2O [a]	Conversion [b] (%)	Yield [c] (%)
Y	1:1:0	19.3	1.5
ZSM-5	1:1:0	22.7	4.2
Beta	1:1:0	25.4	8.2
	1:1:1	27.2	7.8
Zn/Beta	1:1:0	95.5	52.8
Fe/Beta	1:1:0	98.2	64.8
Cu/Beta	1:1:0	85.2	35.4
Mn/Beta	1:1:0	77.6	28.6
Ni/Beta	1:1:0	100	83.1

Reaction condition: the mixtures of ADA (1 mmol) and excessive aniline (4 mmol) react for 5 min under continuous microwave irradiation. [a] the weight ratio of ADA:catalyst:H_2O; [b] conversion of ADA; [c] quinoline determined by GC; based on ADA.

Table 2 The reaction of ADA with different substituted aniline

anilines	Product	Yield of quinolines (%)
		58.4
		41.3
		66.8
		25.8
		19.4
		31.3
		65.3
		57.2
		32.1
		27.9
		29.6
		31.5

Reaction condition: the mixtures of ADA (1 mmol) and anilines (4 mmol) react for 5 min under continuous microwave irradiation over Ni/Beta catalyst; the weight ratio of ADA:catalyst= 1:1.

Figure captions

Fig. 1 The effect of microwave time for quinoline yield over different catalysts.

Fig. 2 the effect of reaction time for product distribution over Beta(**I**) and Ni/Beta(**II**) catalyst.

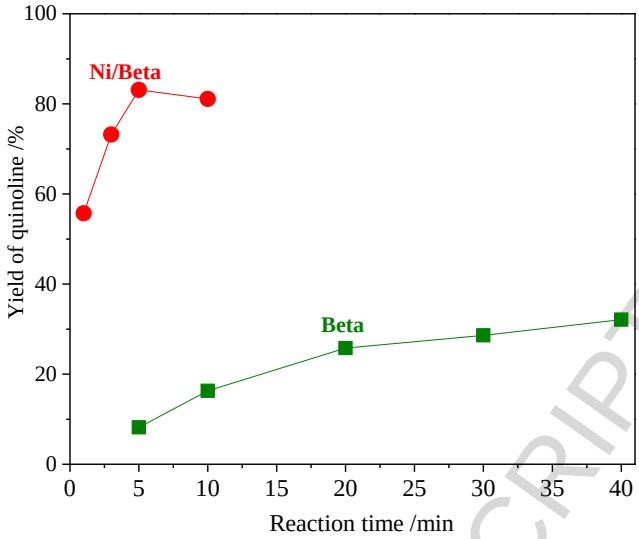


Fig. 1 The effect of microwave time for quinoline yield over different catalysts Reaction condition: the mixtures of ADA (1 mmol) and excessive aniline (4 mmol) react for under continuous microwave irradiation.

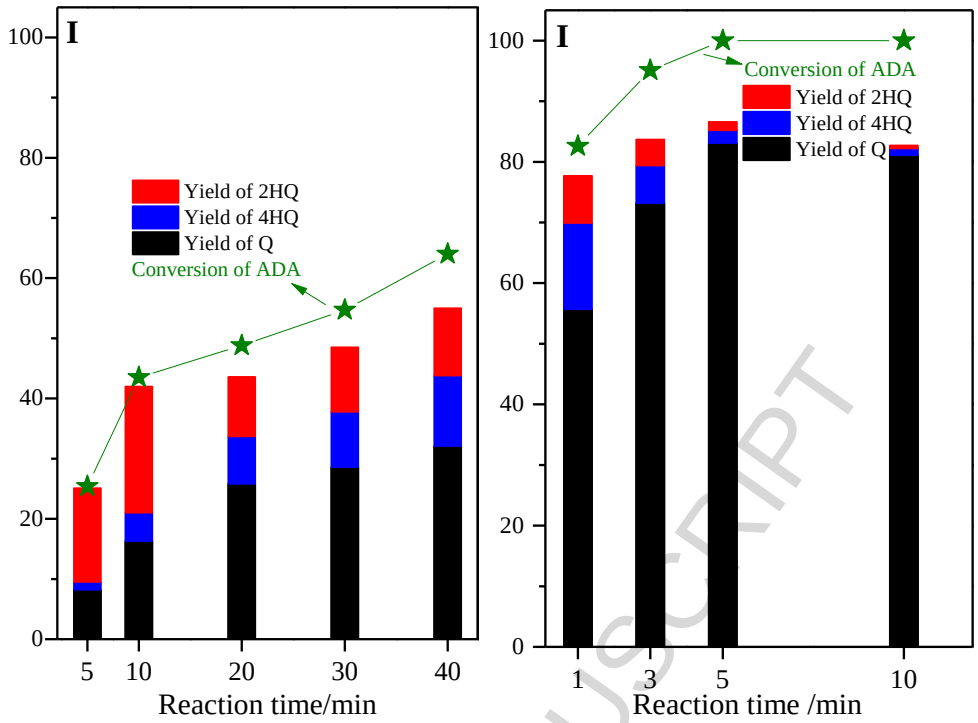
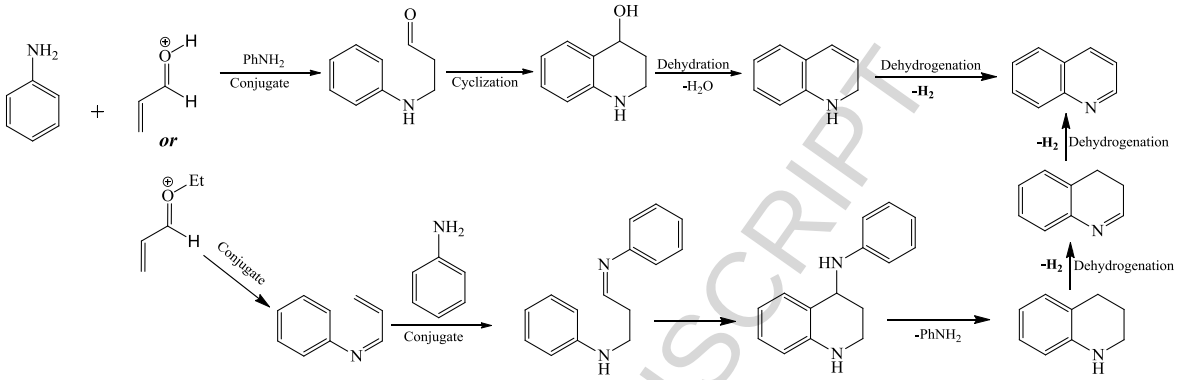
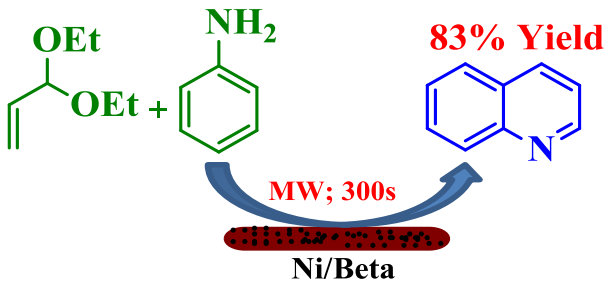


Fig. 2 the effect of reaction time for product distribution over Beta(**I**) and Ni/Beta(**II**) catalyst Reaction condition: the mixtures of ADA (1 mmol) and excessive aniline (4 mmol) react for under continuous microwave irradiation. Q, 2HQ and 4HQ correspond to quinoline, dihydroquinoline and tetrahydroquinoline, respectively.

Scheme captions

Scheme 1. The plausible reaction pathway to form quinoline from aniline and ADA under microwave irradiation.

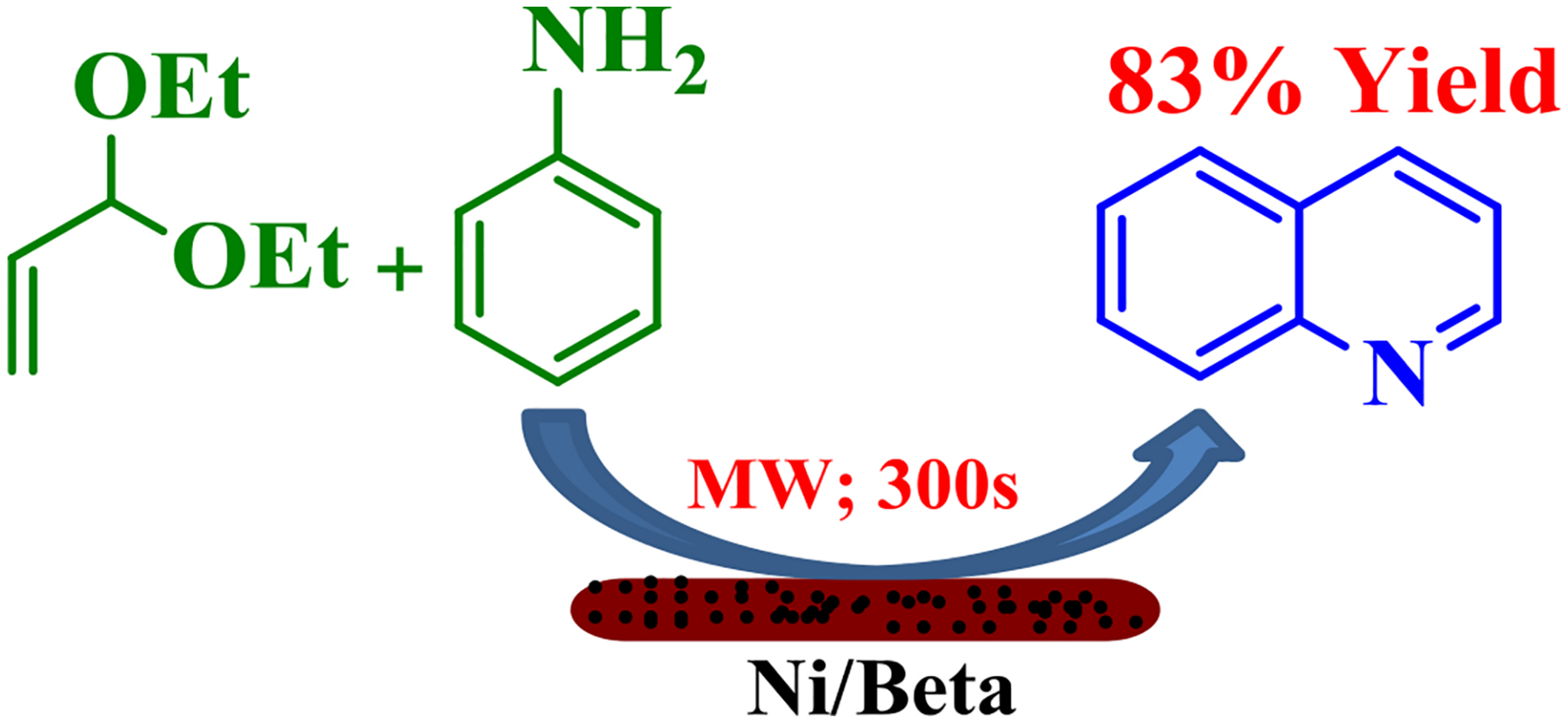




Graphical Abstract

Highlights

- A facile and solvent-free microwave-assisted approach to quinoline was developed.
- An mild, ecofriendly and low-cost zeolite-base catalyst of Ni/Beta was employed.
- the 83% yield of quinoline was obtained at a short microwave time.
- The addition of Ni significantly accelerated dehydrogenation rate during reaction.



Graphics Abstract

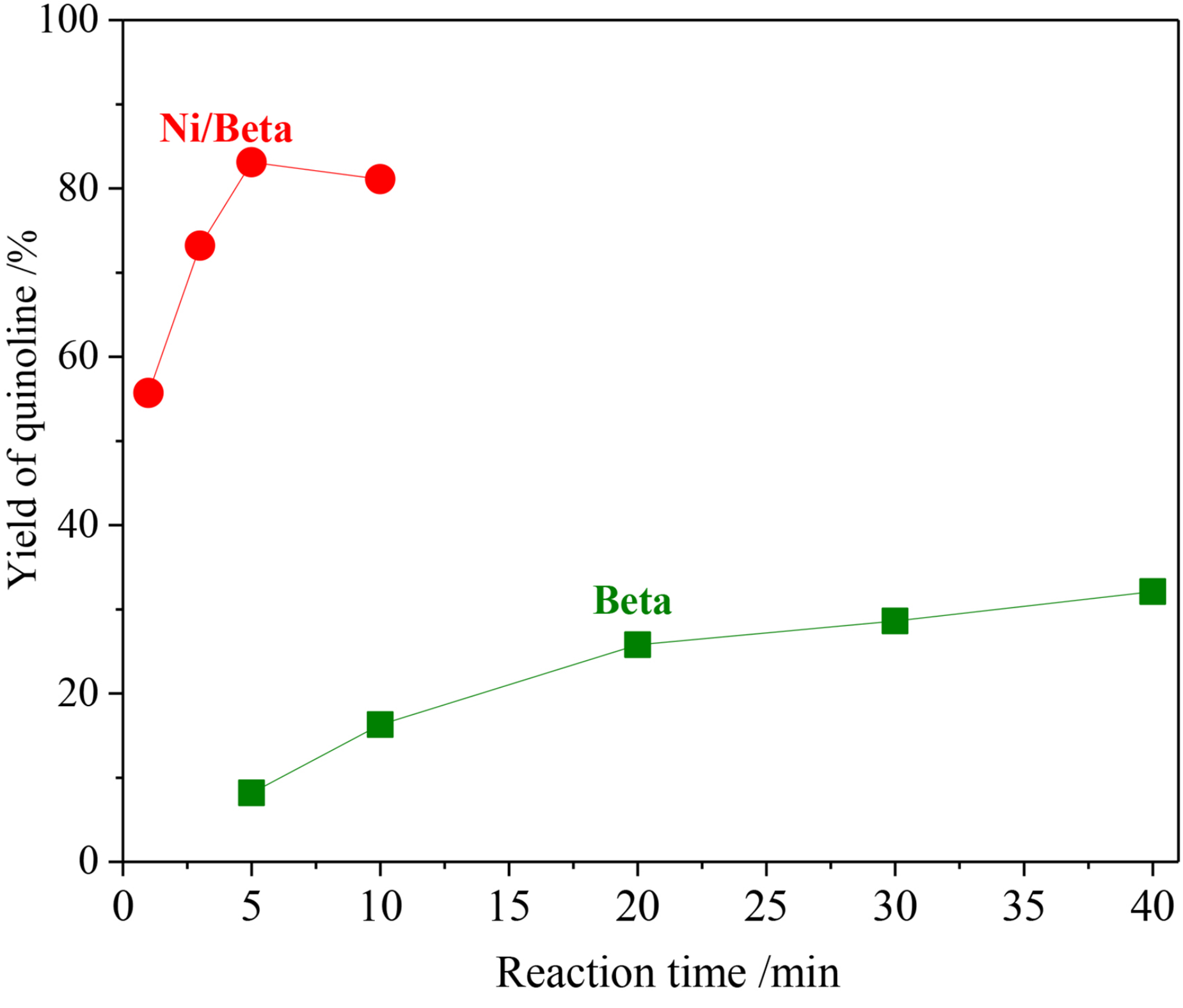

Ni/Beta
Beta
Yield of quinoline /%
Reaction time /min
0
20
40
60
80
100
0
5
10
15
20
25
30
35
40

Figure 1

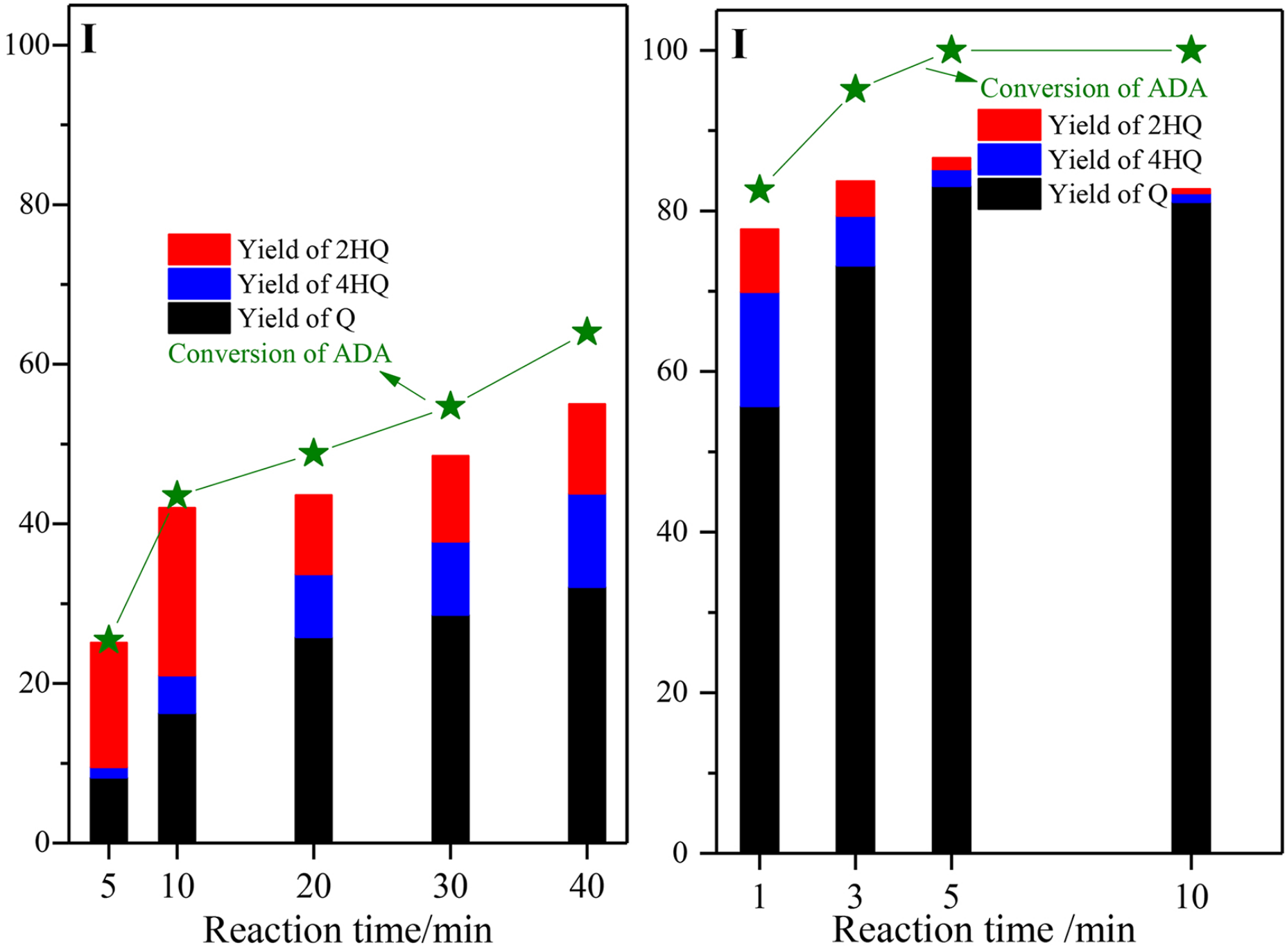

I
100
80
60
40
20
0
Yield of 2HQ
Yield of 4HQ
Yield of Q
Conversion of ADA
5
10
20
30
40
Reaction time/min
I
100
80
60
40
20
0
Conversion of ADA
Yield of 2HQ
Yield of 4HQ
Yield of Q
1
3
5
10
Reaction time /min

Figure 2