Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c9dt01196j

Received 20th March 2019, Accepted 8th July 2019 DOI: 10.1039/c9dt01196j

rsc.li/dalton

1. Introduction

Aminocyclization of ketones with ammonia (NH_3), which is a building block chemical, is an important reaction in synthetic organic chemistry and medicinal chemistry to produce pyridine-based heterocyclic compounds, such as octahydroacridine and its derivatives, which are mainly used as the starting materials for the synthesis of biologically active compounds, dyes, drugs and alkaloids.^{1–3}

Many conventional methods are used for the synthesis of octahydroacridines, as noted in literature.^{4–6} Several homogeneous synthetic methods have not only several multi-step synthesis procedures under expensive catalytic methods but the long durations are also required for recovering the used catalysts after the completion of the reaction. For example, the

Selective synthesis of octahydroacridines and diannelated pyridines over zinc-containing mesoporous aluminosilicate molecular sieve catalysts[†]

Manickam Selvaraj 🝺 * and Mohammed A. Assiri

We demonstrate a very eco-friendly and single-step catalytic method for the highly selective synthesis of 1,2,3,4,5,6,7,8-octahydroacridine (OHA) by the vapour phase aminocyclization of cyclohexanone (Cy=O) with a mixture of formaldehyde (HCHO) and ammonia (NH₃) over mesoporous bimetallic ZnAlMCM-41 (ZnAl-41) molecular sieves as efficient catalysts, which were synthesised by a simple basic hydrothermal method. To find optimum parameters for the synthesis of OHA, different reaction parameters, such as temperature, time on stream (TOS), weight hourly space velocity (WHSV), and feed molar ratios of Cy=O: HCHO: NH₃, have been extensively studied. The used ZnAl-41 catalysts were treated by washing and calcination to recover the recyclable catalysts which were then reused in these reactions to study their catalytic abilities. To selectively synthesize a variety of pyridine compounds, the active mesoporous catalysts, namely, ZnAl-41(75) and recyclable ZnAl-41(75), with different reaction parameters, were extensively used in the vapour phase aminocyclization reaction with different aldehydes and cycloketones, and produced excellent product selectivities, e.g., 9-alkyl substituted octahydroacridines (9-ASOHAs) and diannelated pyridines (DAPs), with good ketone conversions. In this catalytic reaction, OHA, 9-ASOHAs and DAPs are the main products and are important as starting materials in the preparation of biologically active compounds, drugs, dyes and alkaloids. It is shown by our remarkable catalytic results that the ZnAl-41(75) catalyst, as an environmentally friendly heterogeneous catalyst, has outstanding catalytic activity in the production of OHA, 9-ASOHAs and DAPs by a single-step synthetic method.

> Bayer research group reported that the Friedlander condensation of cyclopentanone and cyclohexanone with β-aminoacrolein produces 2,3-fused pyridines.⁶ The synthesis of octahydrophenanthridines was also carried out using bicyclic aromatic and aliphatic dienamides, which was a multi-step procedure, involved corrosive reagents and a homogeneous catalytic system.⁶ All the catalytic systems cause large amounts of waste production with a low amount of major product selectivity. Homogenous catalytic system causes many problems concerning undesirable side products formed using high amounts of raw chemicals, produces high corrosiveness and has several steps to recover the main product. In addition, in the chemical industry, homogenous catalytic materials are unable to be recycled and thus are highly non-ecofriendly. Heterogeneous catalytic chemistry can play a key role in achieving the major goals of 'green chemistry': producing the main product with a higher selectivity, reducing by-products to a trace number, promoting the conversion of large amounts of starting materials used in catalytic reactions, and replacing hazardous and stoichiometric reagents by green catalytic materials which can be



View Article Online

Department of Chemistry, King Khalid University, Faculty of Science, P.O. Box 9004, Abha 61413, Saudi Arabia. E-mail: mselvaraj@kku.edu.sa; Fax: +966 17 241 7637 †Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9dt01196j

Paper

easily recovered from the final reaction mixture and used as recyclable catalysts. Recent research has been highly focused on traditional homogeneous catalysts being replaced by green heterogeneous mesoporous catalysts. Therefore, heterogeneous catalytic materials were used in the production of octahydroacridine and its derivatives. However, microporous zeolites used in the vapour phase cyclization reaction produce several by-products along with the main product, and complicated and expensive processes might be needed to separate the main product from the several by-products.⁷

Generally, green catalytic reactions minimise environmental threats and maximise economic benefits. To supply the great demand in the fine chemical industry, highly suitable solid acid catalysts with a large number of catalytic active sites have been used under mild reaction conditions without employing toxic materials. The Kresge research group, in 1992, discovered well-ordered hexagonal mesoporous materials that have large surface areas, large pore sizes and large pore volumes, which have been used in catalysis, adsorption, controlled drug delivery, energy and environmental applications.8 However, till date, pure mesoporous silica molecular sieves have not been majorly used as catalysts or catalyst supports in chemical industry for bulk molecule conversion due to the limitations of acidity and poor hydrothermal stability, because their thin amorphous silica pore walls are easily destroyed in boiling water and steam through their fast hydrolysis reaction. Thus, enormous amounts of heteroatomic species incorporated into the mesoporous silica walls improve the surface acidity with enhanced hydrothermal stability and produce abundant superior catalytic active sites.⁹⁻¹¹ Compared to zeolites, the synthesised mesoporous catalysts have a lower content of acid sites, but their uniformly hexagonal pores enhance the production of octahydroacridine derivatives.12,13

In 2004, Ratnamala et al. used microporous and mesoporous catalysts for the synthesis of OHA by the vapour phase cyclization reaction of Cy=O, HCHO and NH₃ for the first time and reported that 3 wt% CeZSM-5 has higher OHA selectivity (92%) and Cy=O conversion (100%) than other microporous and mesoporous catalysts, because the Ce3+ ions produce more acid sites uniformly dispersed on the surfaces of pore channels.¹² In 2007, liquid phase cyclization reactions over many molecular sieve catalysts, introduced by Krishna Mohan et al., produced OHA, with a lower selectivity because the liquid phase autoclavation system is only suitable for the synthesis of 1,2,3,4,7,8,9,10-octahydrophenanthridine (OHP) and its derivatives, whereas high amounts of catalysts and a toxic solvent (methanol) were used for the liquid phase reactions.¹⁴ However, the selectivity for OHA and its derivatives increases on increasing the temperature from 423 to 473 K in the vapour phase cyclization reaction using mesoporous aluminosilicate catalysts, as reported in literature.¹³ On the basis of the above research accounts, we used ZnAl-41 catalysts in an eco-friendly, single-step aminocyclization method for the selective synthesis of OHA and its derivatives.

The 9-ASOHAs and DAPs are very important drug intermediates, and valuable synthetic templates for the preparation of new drug chemicals in pharmaceutical industries, and potent anti-inflammatory agents, anti-bacterial agents, inhibitors of gastric acid secretion and calcium channel blockers.^{15–18} However, conventional methods require many steps for the synthesis of 9-ASOHAs and DAPs^{19,20} and produce low yields. Accordingly, we decided to use an ecofriendly catalytic system, which is highly desirable as a singlestep synthetic method, with green routes in the selective synthesis of 9-ASOHAs and DAPs.

Selvaraj et al., for the first time, produced the mesoporous ZnAl-41 catalysts with the details of their physio-chemical characterization.²¹ The ZnAl-41 catalysts have been widely used as promising heterogeneous solid acid catalysts in alkylation,^{21a,22} cyclization²³ and Prins condensation²⁴ for the selective synthesis of valuable fine chemicals by the routes of green heterogeneous catalytic chemistry. To the best of our knowledge, a single-step synthesis of OHA, 9-ASOHAs and DAPs has not been carried out using the mesoporous ZnAl-41 molecular sieve catalysts. Our present investigation presents a unique, eco-friendly and simple method for the selective synthesis of OHA, 9-ASOHAs and DAPs using low cost reactants under a single-step vapour phase method; the true heterogeneous catalysts, ZnAl-41, have been used for the first time in this catalyst system. The catalytic results obtained over ZnAl-41 catalysts for the selective synthesis of OHA, 9-ASOHAs and DAPs were correlated and compared with those for other solid catalysts, such as AlMCM-41(Al-41), ZnMCM-41 (Zn-41), USY, Hβ, HZSM-5 and H-mordenite.

2. Experimental

A variety of mesoporous catalysts, namely bimetallic ZnAl-41 mesoporous catalysts ($n_{\rm Si}/(n_{\rm Zn} + n_{\rm Al}) = 75$, 151, 228, 304 and 380), monometallic mesoporous catalysts Al-41 ($n_{\rm Si}/n_{\rm Al} = 21$) and Zn-41 ($n_{\rm Si}/n_{\rm Zn} = 21$), and mesoporous MCM-41 silica, were synthesized and characterized according to the procedure previously published by Selvaraj *et al.*²¹ For comparison studies, H β ($n_{\rm Si}/n_{\rm Al} = 20$, Strem), HY ($n_{\rm Si}/n_{\rm Al} = 2.9$, PQ), H-ZSM-5 ($n_{\rm Si}/n_{\rm Al} = 30$, PQ) and H-mordenite ($n_{\rm Si}/n_{\rm Al} = 20$, PQ) were commercially purchased. Prior to performing the catalytic reactions, the purchased zeolite catalysts were heat-treated at 473 K in air for 6 h to remove the moisture on the surfaces of active sites.

All catalytic experiments for the vapour phase aminocyclization reaction were carried out in a fixed-bed vertical flow reactor (20 mm diameter) with a continuous down flow. The catalyst bed temperature was measured with a thermocouple placed in the middle of the catalyst bed. Typically, prior to the reaction, the mesoporous solid acid catalytic material (2 g) was activated at 773 K in flowing air for 10 h, followed by cooling to the reaction temperature (450 K) under nitrogen. After an hour, the reactant mixture of Cy=O, (>99.0% ACS reagent, Sigma-Aldrich) and HCHO (37 wt% in H₂O, Sigma-Aldrich) at the desired feed molar ratio and WHSV (obtained by dividing the mass flow of the reactant by the mass of catalyst) were fed

into the reactor using a dual syringe pump (Harvard Apparatus). A desired amount of ammonia gas was also fed through a manometer (calibrated with flow meter) to the catalytic reactor. The condensed liquid products obtained from the gaseous products were collected at different times, analysed by gas chromatography using 10% SE-30 columns, and confirmed using a combined gas chromatography-mass spectrometry system (GC-MS, Hewlett G1800A). The products were purified by column chromatography over a suitable silica gel (100-200 mesh) using 2-10% ethyl acetate and hexane as the eluent. The vapour phase aminocyclization reaction was further carried out using a variety of aldehvdes, namely, acetaldehyde (≥99.5%), propionaldehyde (97%), butyraldehyde $(\geq 99.5\%)$, isobutyraldehyde $(\geq 99\%)$ and valeraldehyde (97%), and different cycloketones, namely, cyclopentanone ($\geq 99\%$) and cycloheptanone (99%). The aldehydes, cycloketones and other chemicals used were purchased from Sigma-Aldrich Inc. (USA). All the products were identified by ¹H NMR and ¹³C NMR spectra and the spectral details are presented in ESI.[†]

The incorporation of Zn and Al ions in ZnAl-41(75) is higher and lower in ZnAl-41(380). To find stability, both bimetallic mesoporous catalysts were reused in the single-step vapour phase synthesis of OHA, 9-ASOHAs and DAPs. In a typical reaction process, from the reaction mixture, the used ZnAl-41(75) catalyst was recovered by washing with acetone several times, and then dried at 393 K. Finally, the ZnAl-41(75) catalyst was calcined at 773 K for 6 h in air for the removal of the formed organics (as coke) and unreacted molecules. The recovered ZnAl-41(75) catalyst was reused in this reaction. The recyclable bimetallic mesoporous catalysts, ZnAl-41(75) with rich Al and Zn ion content and ZnAl-41(380) with low Zn and Al ion content, were regenerated before applying to the catalytic reactions. A similar reaction procedure was used for the recyclable ZnAl-41(75) catalyst for the synthesis of 9-ASOHAs and DAPs. After completion of the reaction, the percentage of Zn and Al ion content of the used catalyst was analyzed by ICP-AES, and the analysis results of GC and GC-MS calculated using standard formulas were used to find the conversions and selectivities.

3. Results and discussion

3.1. Characterization of ZnAl-41

The simple basic hydrothermal method is an eco-friendly method that has been used for the synthesis of a variety of mesoporous catalysts, such as bimetallic mesoporous ZnAl-41 catalysts, monometallic mesoporous catalysts like Al-41(21) and Zn-41(21), and pure mesoporous MCM-41. Relevant sophisticated instrumental techniques were used for the characterization of the synthesised catalysts, according to the procedure published by Selvaraj *et al.*²¹ The XRD results (Fig. 1S†) of several mesoporous catalysts such as Al-41(21) and Zn-41(21), and MCM-41, confirm their mesoporous nature. When the metal-ion content is increased, the decrease in structural pro-

perties, namely *d*-spacing value (d_{100}) and unit cell parameter (a_0) , was also investigated, as shown in Table 1S.[†] Fig. 2S[†] shows that large amounts of Zn and Al ions, which can be confirmed by the intensity of the corresponding FTIR absorption peaks, are highly incorporated into mesoporous silica walls. In addition, the intensity of the FTIR adsorption peaks with the shift in wavenumbers shows that the bimetallic ZnAl-41 catalysts have higher antisymmetric Si-O-Si vibration bands (1096 cm^{-1}) than the monometallic catalysts Al-41 (1083 cm⁻¹) and Zn-41 (1085 cm^{-1}). The incorporation of the larger ionic radii of Zn and Al leads to an increase in wall thickness, as described in literature.²¹ ICP-AES results confirm that the Zn and Al ion contents on the surface of inner pore walls are mostly constant before and after the synthesis of OHA, 9-ASOHAs and DAPs, as shown in Table 1S.† Although the textural properties of ZnAl-41(75) are smaller than those of the other ZnAl-41 catalysts (Table 1S[†]), the number of acid sites of ZnAl-41(75) are higher than that in other mesoporous catalysts, as shown in Table 2S and Fig. 3S,† due to the increase in the number of zinc ions.²¹ All the calcined ZnAl-41 catalysts, as confirmed by SEM studies,²¹ have the micellar rod-like hexagonal shape (Fig. 4S[†]). The hexagonal symmetry and uniform pore channels were clearly identified by the TEM studies, as shown in the TEM image (Fig. 5S[†]) of ZnAl-41(75), indicating that the ZnAl-41 catalysts have uniform mesostructures that have been also confirmed by the results of XRD patterns.²¹

3.2. Selective synthesis of OHA

The characterized mesoporous solid acid catalysts, namely bimetallic ZnAl-41 catalysts and monometallic mesoporous catalysts Al-41(21) and Zn-41(21), were used in the vapour phase aminocyclization of Cy=O with a mixture of HCHO and NH₃ in a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃) at 1 h⁻¹ WHSV at a temperature of 613 K for 1 h TOS, as shown in Table 1. The purchased microporous catalysts, after removal of moisture by calcination, were also used in this reaction under

Table 1 Single step synthesis of OHA over various types of catalysts^a

			Selectivity (%)		
Catalysts	Pore size (Å)	of Cy=O (%)	OHA	DCA	MOHA
ZnAl-41(75)	22.8	98.0	95.0	3.0	2.0
ZnAl-41(151)	25.6	81.3	87.4	7.0	5.6
ZnAl-41(228)	27.0	73.4	66.7	26.1	7.2
ZnAl-41(304)	29.3	65.6	58.9	19.6	$3.8(17.7)^{b}$
ZnAl-41(380)	32.2	57.6	49.5	12.5	$2.5(35.5)^{b}$
HY (2.6)	7.4	72.4	63.4	9.5	$6.2(20.9)^{b}$
Ηβ (20)	7.6×5.4	81.0	68.9	7.4	$15.3(8.4)^{b}$
H-mordenite (20)	7.1	55.0	49.8	4.5	$3.0(42.7)^{b}$
HZSM-5(15)	5.4	83.4	73.2	7.2	$11.5(8.1)^{b}$
Al-41(21)	27.5	79.6	65.6	17.9	$7.8(8.7)^{b}$
Zn-41(21)	27.3	63.5	26.4	65.6	$2.1(8.0)^{b}$
MCM-41	29.3	9.2	7.5	4.0	$1.0(87.5)^{c}$

^{*a*} Reaction conditions: 2 g of catalyst, feed molar ratio of Cy= $O:HCHO:NH_3 = 2:1:3$, T = 613 K, WHSV = 1 h⁻¹, TOS = 2 h. ^{*b*} Trace amounts of cyclohexylamine and aminooctahydroacridines with other unidentified products. ^{*c*} Unreacted reactants.



the same reaction conditions noted in Table 1. In this aminocyclization reaction, OHA is primarily produced by an intramolecular aromatization of the primary product intermediate, 1,2,3,4,5,6,7,8,9,10-decahydroacridine, as shown in Scheme 1. In addition to the byproduct 9-methyl-1,2,3,4,5,6,7,8,-octahydroacridine (MOHA) produced by acid catalyzed methylation of OHA, dicyclohexylamine (DCA) is also formed by direct amination and condensation of cyclohexanones (Cy=Os) with NH₃, while OHP forms with low selectivity at low reaction temperature (513 K) because vapour phase aminocyclization was not favoured. Trace amounts of cyclohexylamine, aminooctahydroacridines and other unidentified products were also observed.

3.3. Selectivity of OHA

As shown in literature, the mesoporous aluminosilicate catalysts Al-MCM-41(15) and Al-MCM-41(30) have been used as convenient solid acid catalysts for syntheses of 1,2,3,4,5,6,7,8octahydroacridin-9-amine (OHAA) and OHA by the vapor phase cyclization method.^{12,13} The mesoporous Al-MCM-41 (30) has 52% OHA selectivity with byproduct selectivities of 5% MOHA and 14% DCA.¹² In contrast, Al-MCM-41(15), in the synthesis of OHAA, has lower OHA selectivity (17%) than Al-MCM-41(30) because OHA in this case is formed by the acid catalysed deamination of OHAA.13 From the above literature results, we found that the mesoporous aluminosilicate catalysts produce OHA with less selectivity; however, this catalyst system leads to a direct condensation product, DCA, with 14% selectivity because the acid sites could not be enhanced to achieve higher selectivity of OHA and its derivatives. We thus introduced bimetallic mesoporous ZnAl-41 catalysts to improve the selectivity of OHA and its derivatives by a single-step vapor phase aminocyclization reaction, because Zn ions incorporated

in mesoporous aluminosilicates are highly favourable catalysts in cyclization, condensation, hydrogenation and dehydrogenation, as reported in literature.²¹⁻²³ The OHA selectivity increases for the series of catalysts as follows: ZnAl-41(75) > $ZnAl-41(151) > HZSM-5(15) > H\beta(20) ZnAl-41(228) > Al-41(21) >$ HY(2.6) > ZnAl-41(304) > H-mordenite(20) > ZnAl-41(380) > Zn-41(21) > MCM-41. The bimetallic ZnAl-41(75) catalyst produces 95% OHA selectivity with 98% Cy=O conversion. Compared to other ZnAl-41 catalysts, ZnAl-41(75) gives higher catalytic activity that increases OHA production with no diffusional constraint, while the incorporation of abundant Zn ions increases the number of acid sites on the inner pore walls of the ZnAl-41 (75) catalyst.²¹ In addition, the OHA selectivity of ZnAl-41(75) is higher than that of Al-41 due to the higher catalytic activity promoted by the abundant Zn ions incorporated on the inner pore walls of Al-41.²¹ However, the HZSM-15(15) catalyst produces higher OHA selectivity than other microporous and mesoporous catalysts, except ZnA-41(75) and ZnAl-41(151), as shown in Table 1, because its acid sites on the pore channels (pore size 5.4 Å) are better adapted for the acid-catalysed aminocyclization of Cy=O compared to those of other catalysts. In contrast, the Zn-41(21) has less OHA selectivity compared to other microporous and mesoporous catalysts used in this catalytic reaction, but increases the DCA yield with a higher selectivity because its acid sites lead to an increase in direct aminocondensation between two Cy=Os with NH₃, as shown in literature.^{12,13,22} It was subsequently noted that HZSM-5 has a higher selectivity of MOHA compared to all the microporous and mesoporous catalysts. Overall, the structural and textural properties of ZnAl-41(75) increase the acid strength, causing high chemisorption between the reactants and active surface of the catalyst to achieve higher OHA selectivity. It is significantly observed that ZnAl-41(75) has higher OHA selectivity than CeZSM-15,¹² because it has higher surface area and more active sites than CeZSM-15. On the basis of the results obtained using different molecular sieve acid catalysts, ZnAl-41 (75) is found to be a promising heterogeneous catalyst in the vapour phase aminocyclization of Cy=O for the highly selective synthesis of OHA.

In conclusion, the above catalytic results confirm that the well-ordered mesoporosity with higher surface area and suitable acid sites highly promoted by the abundant Zn and Al ions plays a significant catalytic role in the synthesis of OHA with higher selectivity.

3.4. Effect of reaction temperature

The vapour phase aminocyclization of Cy=O was carried out at different reaction temperatures with a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃) at 1 h⁻¹ WHSV for 2 h TOS over ZnAl-41(75), as shown in Fig. 1, to explore the effects of Cy=O conversion and the product selectivity. On increasing the temperature from 513 to 613 K, the Cy=O conversion and OHA selectivity increase, whereas the selectivities for by-products OHP, DCA and MOHA decrease. Particularly, for the synthesis of OHP with higher selectivity, the liquid phase autoclavation method is highly suitable, but a vapour phase catalytic system is not favoured, as explained clearly in literature.¹⁴ The Cy=O conversion and OHA selectivity decrease when the reaction temperature further increases from 613 to 653 K because a few active sites on the inner pore walls of the catalysts are screened by coke formation from unreacted reactants, which cause sintering and poisoning, resulting in deactivation, as described in literature.²⁵ At low reaction temperature (<613 K), the chemisorption between the reactants and the Brønsted acid sites of catalysts decreases. In this case, the byproduct formation of OHP, DCA and MOHA increases. Interestingly, we found from the catalysis results that the best reaction temperature is 613 K, which is highly suitable to achieve higher conver-



Fig. 1 Effect of reaction temperature over ZnAl-41(75). Reaction conditions: 2 g of catalyst, feed molar ratio of Cy=O:HCHO:NH₃ = 2:1:3, WHSV = 1 h^{-1} , TOS = 2 h.

sion of Cy=O as well as OHA selectivity. The active sites of ZnA-41(75) at 613 K for 2 h TOS at 1 h^{-1} WHSV might not be reversible, and could be confirmed by the studies of the acidity measurements and hydrothermal stability.²¹

3.5. Effect of time on stream (TOS)

For finding the effects of Cy=O conversion and product selectivity, the vapour phase aminocyclization of Cy=O with different times on stream (TOSs) in a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃) at 613 K over ZnAl-41(75) is displayed in Fig. 2. When the stream time (TOS) is increased from 0.5 to 2 h, the Cy=O conversion and OHA selectivity increase with the decrease in the selectivities for by-products, DCA and MOHA. The low TOS (<1.5 h) is favourable for the acid-catalysed methylation with OHA to form MOHA and causes a direct condensation of Cy=Os with NH₃ to produce DCA. After 2 h TOS, the Cy=O conversion and product selectivity gradually decrease due to the formation of heavy coke, which screens the active sites, on the pore walls of the catalyst caused by increasing the stream time of the reactor. The catalysis results obtained under the reaction conditions remarkably found that the best TOS is 2 h, which leads to 98% Cy=O conversion and 95% OHA selectivity, as shown in Fig. 2.

3.6. Effect of Cy=O, HCHO and NH₃ ratio

To investigate the best feed molar ratio of Cy=O:HCHO:NH₃ for the highly selective synthesis of OHA, the vapour phase aminocyclization of Cy=O was conducted with a variety of feed molar ratios of Cy=O:HCHO:NH₃ at 613 K for 2 h TOS at 1 h⁻¹ WHSV over ZnAl-41(75), as shown in Fig. 3. When this reaction is carried out with a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃), outstandingly, 98% Cy=O conversion and 95% OHA selectivity are observed. Moreover, the Cy=O conversion and OHA selectivity at this feed molar ratio are higher than that of other feed molar ratios because of the greater chemisorption that makes an equilibrium between the



Fig. 2 Effect of TOS over ZnAl-41(75). Reaction conditions: 2 g of catalyst, feed molar ratio of Cy=O: HCHO: NH₃ = 2:1:3, WHSV = 1 h⁻¹, T = 613 K.



Fig. 3 Effect of the feed molar ratios of Cy=O:HCHO:NH₃ over ZnAl-41(75). Reaction conditions: 2 g of catalyst, WHSV = 1 h⁻¹, T = 613 K, TOS = 2 h.

amounts of reactant and the acid sites created on the surfaces of pore walls by the active species of Zn and Al of ZnAl-41(75). The decrease in OHA selectivity is clearly observed in the feed molar ratios of 2:1:2, 2:1:5 and 2:2:5, while at the same feed molar ratios, the decrease in Cy=O conversion is also observed because of the increase in by-product selectivity. Due to the increase in the concentrations of HCHO and NH₃, the formation of DCA with 18-25% selectivity is observed in the feed molar ratios of 2:1:2 and 2:1:5, while MOHA selectivity (10-30%) increases in the feed molar ratios of 2:1:2 and 2:2:5. The selectivity of byproducts, such as DCA and MOHA, is higher compared to that obtained with the feed molar ratio of 2:1:3 because the ratios of the reactants may be matched with the suitable chemisorption of Brønsted acid sites on the inner pore wall surface of the catalyst and could be highly favoured for the direct condensation of Cy=Os with NH₃ to produce DCA and for the acid-catalysed methylation of OHA in the preparation of MOHA. The selectivity of all products such as OHA, DCA and MOHA with Cy=O conversion decreases in a feed molar ratio of 2:1:1 due to the uneven ratios of reactants that form coke on the surfaces of the catalyst with a sintering effect, which screens the active sites of the catalyst, resulting in deactivation.²⁵ The effects of the feed ratio display clearly that 2:1:3 feed molar ratio (Cy=O:HCHO:NH₃) is an optimum ratio among all the ratios tested for the highly selective synthesis of OHA.

3.7. Effect of weight hourly space velocity (WHSV)

A single-step synthesis of OHA was carried out by the vapour phase aminocyclization of Cy=O at various space velocities (WHSVs) with a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃) at 613 K for 2 h TOS over ZnAl-41(75), as shown in Fig. 4, to investigate the effect of product selectivity along with Cy=O conversion. When the WHSV was increased from 0.5 to 1 h⁻¹, the OHA selectivity increased with the



Fig. 4 Effect of WHSVs over ZnAl-41(75). Reaction conditions: 2 g of catalyst, feed molar ratio of Cy=O:HCHO:NH₃ = 2:1:3, TOS = 2 h, T = 613 K.

increase in Cy=O conversion. Following this, the Cy=O conversion and OHA selectivity gradually decreased until 2 h⁻¹ WHSV, whereas the formation of byproducts such as DCA and MOHA with ~10–20% selectivity can also be observed at 0.5 h⁻¹ WHSV because the contact times (before and after 1 h⁻¹ WHSV) were not suitable to lead to further reactions, such as cyclization and aromatization. After 2 h⁻¹ WHSV, the OHA decomposes with the formation of heavy coke because of contact time. Based on the effect of the space velocities (WHSV), we clearly find that the best contact time is 1 h⁻¹ WHSV for the selective synthesis of OHA.

3.8. Recyclability

Among the bimetallic ZnAl-41 catalysts evaluated for the single-step aminocyclization, ZnAl-41(75) and ZnAl-41(380) have correspondingly the highest and lowest OHA selectivities. The evaluation of reusability for the bimetallic ZnAl-41 catalysts was thus carried out under the reaction conditions noted in Table 2 to determine their catalytic stabilities. Typically, the catalysts used for this reaction are affected from the loss of catalytic activity because most of the active sites are blocked by unreacted organics, which is one of the factors contributing to the sintering effect on the catalyst surface. Prior to reuse, the catalysts were chemically treated and calcined for regeneration, as explained in the procedure reported by Selvaraj et al.²² The used catalysts were washed several times with acetone, dried overnight at 393 K and further calcined at 773 K for 6 h in air for the removal of organics and unreacted organic molecules. The regenerated catalysts were recycled in this reaction, as described in Table 2. All the regenerated catalysts were recovered using the above procedure before applying to each run. In the first two runs, the increase in Cy=O conversion and a slight increase in OHA selectivity were observed. The results of the first and second runs confirm clearly that small numbers of active sites on the inner pore surfaces of ZnAl-41

Table 2 Recycling of ZnAl-41(75) and ZnAl-41(380)^a

	_		- ·	Selectivity (%)		
Catalysts	Pore size (Å)	Run	of Cy=O (%)	OHA	DCA	MOHA
ZnAl-41(75)	22.8	1	98	96	2.0	2.0
ZnAl-41(75)	22.9	2	99	97	2.0	1.0
ZnAl-41(75)	22.9	3	100	97.5	1.5	1.0
ZnAl-41(75)	22.9	4	100	97.5	1.5	1.0
ZnAl-41(380)	31.5	1	57.6	49.5	12.5	$3.0(35)^{b}$
ZnAl-41(380)	31.5	2	57.7	49.6	12.6	$4.5(33.3)^{l}$
ZnAl-41(380)	31.5	3	57.7	49.6	12.6	$4.6(33.2)^{l}$
ZnAl-41(380)	31.5	4	57.7	49.6	12.6	$4.6(33.2)^{l}$

^{*a*} Reaction conditions: 2 g of catalyst, feed molar ratio of Cy= $O:HCHO:NH_3 = 2:1:3$, T = 613 K, WHSV = 1 h⁻¹, TOS = 2 h. ^{*b*} Trace amounts of cyclohexylamine and aminooctahydroacridines with other unidentified products.

(75) were screened/blocked by the non-framework octahedral aluminium and zinc oxides that are completely removed after the washing and calcination processes. After the third and fourth runs, the Cy=O conversion and OHA selectivity remain constant, indicating that the incorporated or substituted active species (Zn- and Al-ions) were not leached, in the present reaction conditions, from the surface of the mesoporous silica matrix, as shown by the ICP-AES results of ZnAl-41(75) after the recycling reactions (Table 1S[†]). The Cy=O conversion and OHA selectivity in ZnAl-41(380) almost remain constant with each cycle, because the low amount of active species can be homogenously incorporated on the inner silica pore walls. The amount of Zn and Al ions in ZnAl-41(380) was also determined by ICP-ACS after the recycling reaction, as shown in Table 1S.† This process is also found to be a true heterogeneous catalytic process.^{26,27} This reaction was also carried out using pure MCM-41 synthesized by the direct basic hydrothermal method.^{21c} In this case, Cy=O (9.2%) forms with a trace amount of product selectivity (Table 1). In conclusion, we are clearly note from all the catalytic results that the bimetallic ZnAl-41(75) is a principal catalyst to obtain higher OHA selectivity by a single-step vapour phase aminocyclization reaction.

3.9. Aminocyclization of cyclohexanone with various aldehydes

To obtain the highly selective synthesis of 9-alkyl substituted OHA derivatives, the ZnAl-41(75) catalyst was used extensively in the single-step vapour phase aminocyclization of cyclohexanone with various aldehydes under the reaction conditions noted in Table 3. In these catalytic reactions, the major products (MOHA, 9-ethyl-1,2,3,4,5,6,7,8-octahydroacridine, 9-propyl-1,2,3,4,5,6,7,8-octahydroacridine, 9-isopropyl-1,2,3,4, 5,6,7,8-octahydroacridine and 9-butyl-1,2,3,4,5,6,7,8-octahydroacridine) and byproducts (6-methyl-1,2,3,4,7,8,9,10-octahydrophenanthridine, 6-ethyl-1,2,3,4,7,8,9,10-octahydrophenanthridine, 6-propyl-1,2,3,4,7,8,9,10-octahydrophenanthridine, 6-isopropyl-1,2,3,4,7,8,9,10-octahydrophenanthridine and 6-butyl-1,2,3,4,7,8,9,10-octahydrophenanthridine) can be produced when the corresponding aldehydes, viz. acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde

and valeraldehyde, are used. At 613 K, the selectivities of 9-ASOHAs and conversions of Cy=O increase compared to the selectivities of 6-alkyl substituted octahydrophenanthridines (6-ASOHPs). However, the selectivities of 9-ASOHAs and conversions of Cy=O decrease at 513 K because the low reaction temperature is highly suitable for the production of 6-ASOHPs, as reported in the literature.¹⁴ The aminocyclization of cyclohexanone with various aldehydes was carried out at 4 h TOS; the selectivities of 9-ASOHAs and conversions of Cy=O gradually decrease due to the formation of heavy coke by increasing the stream time of reactor, and the coke screens the active sites on the pore walls of the catalyst of ZnAl-41(75). When the aminocyclization reaction is carried out at 0.5 h^{-1} WHSV, the conversions of Cy=O as well as selectivities of 9-ASOHAs decrease because the contact time is not long enough to covert the 9-ASOHAs completely from the reactants whereas the byproducts could not be also formed by cyclization and aromatization. When the amounts of aldehydes and NH3 are increased, as in a feed ratio of 2:2:5 (Table 3), the selectivities of 9-ASOHAs decrease with the decrease in conversions of Cy=O because an uneven ratio of reactants produces heavy coke under the reaction conditions that screens the active sites on the surface of the catalyst, resulting in deactivation by the sintering effect.²⁵ The conversions of Cy=O and selectivities of 9-ASOHAs are similar in recycled ZnAl-41(75) and calcined ZnAl-41(75) because the active sites on the surface of the catalyst did not leach when the recyclable ZnAl-41(75) catalyst was used up to 4 runs. This is confirmed as the active species, Zn and Al, in recyclable ZnAl-41 (75) are in irreversible manner, according to ICP-AES studies. Overall, an important fact in the catalytic reactions is that the conversions of Cy=O and selectivities of 9-ASOHAs decrease when the alkyl chain length in aldehydes is increased, as reported in elsewhere.7,14

3.10. Aminocyclization with various cyclic ketones

A single-step vapour phase aminocyclization reaction was carried out using different cyclic ketones over ZnAl-41(75) under the reaction conditions noted in Table 4. For the highly selective synthesis of 1,2,3,5,6,7-hexahydrodicyclopenta[b,e] pyridine (HHDCPP) and 1,2,3,4,5,7,8,9,10,11-decahydrodicyclohepta[b,e]pyridine (DHDCHP), the aminocyclization reactions were carried out using the corresponding ketones, namely, cyclopentanone and cycloheptanone, using ZnAl-41(75) under the reaction conditions noted in Table 4. At 613 K, the ketone conversions and selectivities of HHDCPP and DHDCHP are higher compared to those of 1,2,3,6,7,8-hexahydrodicyclopenta [b,d]pyridine (HHDCP[b,d]P) and 1,2,3,4,5,8,9,10,11,12-decahydrodicyclohepta[*b*,*d*]pyridine (DHDCH[*b*,*d*]P). However, compared to HHDCPP and DHDCHP, the selectivities of HHDCP [b,d]P and DHDCH[b,d]P increase at 513 K because the low reaction temperature is favourable for the synthesis of these products, as indicated in previous literature.¹⁴ When the aminocyclization reactions with various ketones were carried out at 4 h TOS, the selectivities of HHDCPP and DHDCHP decrease with the decrease in ketone conversions because heavy coke can be formed on the inner pore walls of ZnAl-41

Dalton Transactions

S. no.	Ketone	Aldehyde	Amine	Product	$T(\mathbf{K})$	Selectivity (%)	Ketone conversion (%)
1	Ö	Ö	Ĥ	Ĥ	513	60	73
			 N	$\wedge \downarrow \wedge$	613	95	98
	ц	н∕ "``н		613^{b}	55	66	
				613 ^c	70	78	
	\sim			~ N ~	613 ^d	52	83
				1,2,3,4,5,6,7,8-octahydroacridine	613^{e}	97.5	100
2	Ö	Ö	Ч	СН ₃	513	61	67
			 N	$\wedge \downarrow \wedge$	613	73	89
		и СН.	н∕ "``н	$ \left(\begin{array}{c} \uparrow \\ \uparrow \end{array} \right) $	613^{b}	47	51
					613 ^c	61	65
	\sim			\sim N \sim	613 ^d	43	71
				9-methyl-1,2,3,4,5,6,7,8-octahydroacridine	613^{e}	73	90
3	Ö	Ö	Ч	_CH ₃	513	52	60
			 N		613	61	85
			н∕ "`_н	\sim	613^{b}	41	43
					613 ^c	49	57
	\sim	CH ₃			613^{d}	33	59
				9-ethyl-1,2,3,4,5,6,7,8-octahydroacridine	613 ^e	61	86
4	Ö	Ö	Ĥ	СНа	513	41	53
			 N		613	52	80
			н∕ "`_н		613^{b}	33	35
					613 ^c	37	43
	\sim	H		\sim N	613^{d}	28	48
		1.30		9-propyl-1,2,3,4,5,6,7,8-octahydroacridine	613 ^e	53	81
5	0	0	Ĥ	H ₃ C、 _C H ₃	513	29	40
	l l			° Y °	613	41	75
	$\langle \rangle$	CH ₃		$\sim \land \sim$	613^{b}	22	28
		H			613 ^c	26	31
\sim	\sim	CH ₃			613^{d}	20	37
				9-isopropyl-1,2,3,4,5,6,7,8-octahydroacridine	613 ^e	42	75
6	0	H	Ĥ	CH ₃	513	15	33
	l I	CH3			613	32	60
	$\langle \rangle$	<u> </u>	⊔∕ ^N ∖⊔	$(\gamma \gamma)$	613^{b}	16	19
	Ĺ				613 ^c	19	22
	\sim			9-hutyl=1 2 3 4 5 6 7 8-octahydroporiding	613^d	17	28
				5-54(y)-1,2,5,4,5,6,7,5-56(a)y0/04010118	613 ^e	32	61

 Table 3
 Aminocyclization of cyclohexanone with various aldehydes^a

^{*a*} Reaction conditions: 2 g of ZnAl-41(75), feed molar ratio of Cy=0 : HCHO : NH₃ = 2 : 1 : 3, WHSV = 1 h⁻¹, TOS = 2 h. ^{*b*} TOS = 4. ^{*c*} WHSV = 0.5 h⁻¹. ^{*d*} Feed ratio: 2 : 2 : 5. ^{*e*} The catalytic results received in 4th run.

S. no.	Ketone	Aldehyde	Amine	Product	$T(\mathbf{K})$	Selectivity (%)	Ketone conversion (%)
1	0	0	Ĥ	Н	513	72	77
	l l				613	89	96
	$\langle \rangle$				613^{b}	66	69
		пп	11 11		613 ^c	61	56
				\bigvee $N^2 \bigvee$	613^{d}	69	60
				1,2,3,5,6,7-hexahydrodicyclopenta[b,e]pyridine	613 ^e	90	97
2	0	Q	Ĥ	Н	513	75	80
	l			\sim \downarrow \sim	613	96	99
	$\langle \rangle$				613^{b}	70	72
		пп			613 ^c	69	61
				\sim N^{-}	613^{d}	76	68
				1,2,3,4,5,7,8,9,10,11-decahydrodicyclohepta[b,e]pyridine	613^{e}	97	100

^{*a*} Reaction conditions: 2 g of ZnAl-41(75), feed molar ratio of Cy=O: HCHO: NH₃ = 2:1:3, WHSV = 1 h⁻¹, TOS = 2 h. ^{*b*} TOS = 4. ^{*c*} WHSV = 0.5 h⁻¹. ^{*d*} Feed ratio: 2:2:5. ^{*e*} The catalytic results received in 4th run.

(75) on increasing the stream time of reactor and the active sites on the pore walls of the ZnAl-41(75) catalyst can be screened by the formation of cokes. At 0.5 h^{-1} WHSV, the

ketone conversions and selectivities of HHDCPP and DHDCHP were low due to the low contact time, which could not convert the main products completely from the reactants, whereas the

byproducts can be easily formed by cyclization and aromatization. As noted in Table 4, in a feed ratio of 2:2:5, the selectivities of HHDCPP and DHDCHP decrease with the decrease in ketone conversions when the amounts of formaldehyde and NH3 are increased, because this ratio of reactants could not evenly react and causes heavy coke formation, which screens the active sites on the surface of catalyst, resulting in deactivation by the sintering effect.²⁵ Prior to reuse ZnAl-41(75), it was treated by washing and calcination processes, using the procedure previously published by Selvaraj et al.,²⁵ to remove the unreacted reactants and moisture on the active sites of the surface of the catalysts. The results show that the catalytic activity of both catalysts, calcined ZnAl-41(75) and recycled ZnAl-41(75), are similar, as shown in Table 4, because the active sites of ZnAl-41(75) were not changed when the recycled ZnAl-41(75) catalyst was used up to 4 runs, as can be confirmed by the contents of Zn and Al species in recycled ZnAl-41(75) based on ICP-AES studies. Overall, an important insight in the catalytic reactions, as we found, is that the ketone conversions and selectivities of HHDCPP and DHDCHP increase when the number of carbons in the cycloketones increased, according to the catalysis results of aminocyclization of different ketones displayed in Table 4.

3.11. Reaction mechanism

On the basis of the major product, OHA, and minor by-products, DCA and MOHA, a plausible reaction mechanism is proposed to clearly explain how the acid sites of bimetallic ZnAl-41 catalysts work in the single-step vapour phase aminocyclization reaction of Cy=O with a mixture of HCHO and NH₃, as shown in Scheme 1. Initially, the carbonyl group of cyclohexanone is protonated by the Brønsted acid site of ZnAl-41 and further reacts with NH₃ to give 1-cyclohexanimine to give an imine, cyclohex-1-enamine, by auto-isomerization caused by the Brønsted acid sites of ZnAl-41. Next, deamination produces 1,2,3,4,5,6,7,8,9,10-decahydroacrdine after an aminocyclization reaction occurs between formaldehyde and two moles of cyclohex-1-enamine. Finally, the major product, OHA, forms by aromatization and dehydrocyclization. In a similar manner, OHP forms at low reaction temperatures. In addition, the formation of by-products DCA and MOHA could be clearly observed by a direct condensation of Cy=Os with NH₃ and acid-catalysed methylation of OHA, as shown in Scheme 1.

Using a similar plausible reaction mechanism over ZnAl-41 (75), the 9-ASOHAs, using different aldehydes with a singlestep aminocyclization of Cy=O, and the DAPs products HHDCPP and DHDCHP, by a single-step aminocyclization reaction with a variety of cycloketones, can be synthesised.

4. Conclusions

The single-step vapour phase aminocyclization reaction is an easy and eco-friendly method to produce OHA over mesoporous and microporous solid acid catalysts. In particular, the selective synthesis of OHA was successfully carried out using bimetallic ZnAl-41 catalysts with highly suitable active sites for the amination of Cy=O with NH₃, heterocyclization reaction of cyclohex-1-enamine with HCHO, and aromatization and dehydrocyclization of 1,2,3,4,5,6,7,8,9,10-decahydroacridine into OHA. Compared with other mesoporous and microporous catalysts, ZnAl-41(75) has higher number of active acid sites on the surface pore walls that can lead to higher catalytic activity in this catalyst system. The results of optimizing reaction parameters revealed that the highest OHA selectivity and Cy=O conversion are obtained at 613 K for 2 h TOS at contact time and 1 h⁻¹ WHSV using a feed molar ratio of 2:1:3 (Cy=O:HCHO:NH₃). The calcined ZnAl-41(75) was successfully used for the synthesis of 9-ASOHAs by a single-step aminocyclization of Cy=O using different aldehydes and for the synthesis of DAPs products, HHDCPP and DHDCHP, by a single-step aminocyclization reaction with a variety of cycloketones. The catalytic activity of recyclable ZnAl-41(75) is similar to that of calcined ZnAl-41(75). On the basis of all the catalysis studies, it is clear that the ZnAl-41(75) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of OHA, 9-ASOHAs and DAPs by the singlestep vapour phase aminocyclization reaction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this study through Large Research Group Project under grant number R.G.P. 2/60/40.

References

- 1 A. Canas-Rodriguez, R. G. Canas and A. Mateo-Bernardo, *Chem. Abstr.*, 1988, **108**, 112191t.
- 2 A. Adrien, *Acridines; their preparation, physical, chemical and biological properties and uses*, Interscience Publishers Ltd., London, 1951.
- 3 R. M. Acheson and L. E. Orgel, *Acridines*, Interscience Publishers Inc., New York, 1956.
- 4 R. P. Thummel and D. K. Kohli, *J. Org. Chem.*, 1977, 42, 2742.
- 5 (a) B. Tabyaoui, T. Aubert, M. Farnier and R. Guilard, Synth. Commun., 1988, 18, 1475; (b) R. S. Monson, D. N. Priest and J. C. Ullrey, Tetrahedron Lett., 1972, 10, 929.
- 6 (a) E. Breitmaier and E. Bayer, Angew. Chem., Int. Ed. Engl., 1969, 8, 765; (b) E. Breitmaier and E. Bayer, Tetrahedron Lett., 1970, 3291; (c) E. Breitmaier, S. Gassenmann and E. Bayer, Tetrahedron, 1970, 26, 5907; (d) A. Couture, C. Bochu and P. Grandclaudon, Tetrahedron Lett., 1989, 30, 6865.

- 7 (a) A. K. Macharla, M. R. Marri, S. Peraka, N. Mameda,
 S. Kodumuri, V. V. K. M. Kandepi and N. Nama, *Catal. Lett.*, 2015, 145, 1922; (b) K. Kamata, Y. Tominaga, A. Torii,
 T. Thiemann and S. Mataka, *Heterocycles*, 1998, 48, 1663.
- 8 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 9 A. Corma, Chem. Rev., 1997, 97, 2373.
- 10 A. Corma, V. Forance, M. T. Navarro and J. Perez-Parients, J. Catal., 1994, 148, 569.
- M. Selvaraj, A. Pandurangan, K. S. Seshadri, P. K. Sinha, V. Krishnasamy and K. B. Lal, *J. Mol. Catal. A: Chem.*, 2002, 186, 173.
- 12 A. Ratnamala, V. D. Kumari, M. Subrahmanyam and N. Archana, *Chem. Commun.*, 2004, 2710.
- 13 A. Ratnamala, K. Lalitha, J. K. Reddy, V. D. Kumari and M. Subrahmanyam, *J. Mol. Catal. A: Chem.*, 2008, 279, 112– 118.
- 14 K. V. V. Krishna Mohan, N. Narender and S. J. Kulkarni, *Microporous Mesoporous Mater.*, 2007, **106**, 229.
- 15 (a) Y. Maruyama, K. Anami and Y. Kotoh, Arzeimittel-Forsch., 1978, 28, 2102; (b) Y. Maruyama, K. Anami, M. Terasawa, K. Goto, T. Imayoshi, Y. Kodobe and Y. Mizushima, Arzeimittel-Forsch., 1981, 31, 1111.
- 16 Y. Rival, G. Grassy and G. Michel, *Chem. Pharm. Bull.*, 1992, 40, 1170.
- J. J. Kaminski, B. Wallmark, C. Briving and B. M. Andersson, *J. Med. Chem.*, 1991, 34, 533.

- 18 P. J. Sanfilippo, M. Urbanski, J. B. Press, B. Dubinsky and J. B. Moore, *J. Med. Chem.*, 1988, **31**, 2221.
- 19 R. P. Thummel and D. K. Kohli, J. Org. Chem., 1977, 421, 2742.
- 20 B. Tabyaoui, T. Aubert, M. Farniar and R. Guilard, *Synth. Commun.*, 1988, **18**, 1475.
- 21 (a) M. Selvaraj, B. R. Min, Y. G. Shul and T. G. Lee, Microporous Mesoporous Mater., 2004, 74, 143;
 (b) M. Selvaraj, S. W. Song and S. Kawi, Microporous Mesoporous Mater., 2008, 110, 472; (c) M. Selvaraj, Ph.D. thesis, Anna University, Chennai, 2002.
- 22 (a) M. Selvaraj and T. G. Lee, *Microporous Mesoporous Mater.*, 2005, 85, 52; (b) M. Selvaraj and P. K. Sinha, *J. Mol. Catal. A: Chem.*, 2007, 264, 44; (c) M. Selvaraj and S. Kawi, *J. Mol. Catal. A: Chem.*, 2007, 265, 250; (d) M. Selvaraj, P. K. Sinha, D. W. Park, I. Kim, S. Kawi and C. S. Ha, *Dalton Trans.*, 2012, 41, 14197.
- 23 (a) M. Selvaraj, B. R. Min, Y. G. Shul and T. G. Lee, *Microporous Mesoporous Mater.*, 2004, 74, 157;
 (b) M. Selvaraj and T. G. Lee, *Microporous Mesoporous Mater.*, 2005, 85, 52.
- 24 M. Selvaraj and S. Kawi, J. Mol. Catal. A: Chem., 2006, 246, 218.
- 25 M. Selvaraj, RSC Adv., 2016, 6, 60983.
- 26 R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, Acc. Chem. Res., 1998, 31, 485.
- 27 J. Dedecek, N. Zilkova and J. Cejka, *Microporous Mesoporous Mater.*, 2001, 44–45, 259.