Catalytic microwave synthesis of biphenyl urea over mesoporous $\text{ZrO}_2\text{-Al}_2\text{O}_3$

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Abstract

Solid acids such as ZrO_2 , Al_2O_3 and $\text{ZrO}_2\text{-Al}_2\text{O}_3$ were prepared and analyzed for their physico-chemical properties like surface acidity and acid site distribution by $\text{NH}_3\text{-TPD}$, crystalline nature by powder XRD, functionality by FT-IR, morphology by TEM and elemental analysis by ICP-OES methods. These solid acids were used as catalysts in the solvent free synthesis of biphenyl urea using microwave irradiation technique starting from aniline and dimethyl carbonate. Surface acidity and the phase of the solid acid were found to have a significant role in the synthesis of biphenyl urea. Up to (98%) yield of biphenyl urea with 100% selectivity was obtained in just 12 min. The activity of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was compared with Mo(VI)/ZrO_2 which is a solid super acid. For comparison, the reactions were also carried out by using conventional heating method. Kinetic studies were carried out to determine energy of activation of the solid acids. These solid acid catalysts were found to be reactivable and reusable when used for up to six reaction cycles.

Keywords Microwave · Modified ZrO_2 · Mesoporous $\text{ZrO}_2\text{-Al}_2\text{O}_3$ · Solid acids

1 Introduction

Metal oxide, especially zirconia based solid acid catalysts have played a vital role as heterogenous catalysts in many industrially important organic transformations [1–3]. It is reported that the mixed oxide of zirconia with alumina (i.e., $\text{ZrO}_2\text{-Al}_2\text{O}_3$) possess higher acidic character than either pure zirconia or pure alumina. i.e., acidity can be increased by incorporating alumina into zirconia⁴. Such mixed oxide form has been used in organic reactions such as esterification, transesterification, condensation, acetylation, etc. [5, 6].

N,N'-diaryl urea are a class of organic compounds which have significant roles in biological and medical applications [7]. These compounds are mainly used in agro-chemical, dye, resin, fibre and pharmaceutical industries [8]. Especially, biphenyl urea (BPU) is studied extensively because of its importance in industries and academics for

the production of carbamates and isocyanates [9]. Normally, BPU and its derivatives are synthesized by using toxic and environmental unfriendly reagents like phosphine, CO, formamides, etc. [10]. Generally, it is prepared by phosgenation route which has a major drawback such as corrosion. Another method is by the reaction between a cyclic carbonic ester with an amine. This method is expensive and is not reliable for industrial level production [11]. The synthesis of BPU and its derivatives over AlPOs, supported MnO catalysts is also reported [7–12]. These methods involve either toxic reagents or consuming reaction times or tedious routes.

In the recent years, high speed microwave irradiation has been used for various applications such as organic synthesis, where the reactions are accelerated by the absorption of microwave energy by the reactant molecules [13, 14]. Microwave-assisted reactions are energy-efficient and quick to synthesize fine chemicals [15]. The literature

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survey revealed that microwave irradiated heating method could be effectively used in industrially important reactions such as transesterification, alkylation, acetylation, coupling, etc. [16–19].

In this article an effort to synthesize biphenyl urea (BPU) over solid acids like ZrO_2 , Al_2O_3 and $\text{ZrO}_2\text{-Al}_2\text{O}_3$ under microwave irradiation condition is made. The solid acids were prepared and analyzed for their surface acidic properties, crystallinity, functionality, morphology and elemental analysis. Optimization of reaction conditions was studied by altering the reaction parameters such as nature of solid acid catalyst, molar ratio of the reactants, amount of the catalyst, reaction temperature and time period. Kinetic studies were carried out to determine energy of activation of the solid acids. A study on the reactivation and reusability of these solid acid catalysts was also carried out.

2 Experimental

2.1 Materials

Zirconyl nitrate, aluminium nitrate nonahydrate, ammonium molybdate, aniline and dimethyl carbonate were supplied by M/S SD Fine Chemicals India Ltd.

2.2 Preparation of ZrO_2 and Al_2O_3

ZrO_2 was prepared by precipitation technique [4, 5] by using 20 g of zirconyl nitrate dissolved in 100 mL of deionised water to obtain a solution. This solution was heated at 353 K for 10 min and precipitation was carried out using ammonia solution (1:1) with stirring. Thus obtained precipitate of Zr(OH)_4 was filtered using a Buchner funnel, washed with deionized water, dried in hot air oven at 393 K for 12 h, finely powdered and calcined at 823 K for 5 h in a furnace. Similarly, pure Al_2O_3 was prepared by using aluminum nitrate.

2.3 Preparation of $\text{ZrO}_2\text{-Al}_2\text{O}_3$

$\text{ZrO}_2\text{-Al}_2\text{O}_3$ consisting of 10%, 20% and 40% ZrO_2 were prepared by using co-precipitation method. Typically, to prepare 40% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, 10.0 g of aluminum nitrate nonahydrate and 2.05 g of zirconyl nitrate were dissolved in 300 mL deionized water and heated to 353 K for 1 h. The

hot solution was filtered for remove any undissolved impurities. The solution was cooled to room temperature and precipitated using 1:1 ammonia solution. The resulting precipitate was filtered using a Buchner funnel, washed with deionized water, dried in hot air oven at 393 K for 12 h, finely powdered and calcined at 823 K for 5 h in a furnace. Similarly, $\text{ZrO}_2\text{-Al}_2\text{O}_3$ consisting of 10% and 20% were prepared.

2.4 Preparation of 5%Mo(VI)/ ZrO_2

4.5 g of zirconyl nitrate and 0.16 g of ammonium molybdate were taken in a china dish and made into a paste. The paste was then dried at 393 K for 12 h in a hot air oven and the obtained solid was finely powdered. The powder was calcinated in a furnace for 5 h at 823 K.

The calcined solid acids such as ZrO_2 , Al_2O_3 , $\text{ZrO}_2\text{-Al}_2\text{O}_3$ (consisting of 10%, 20%, 40% ZrO_2) and 5%Mo(VI)/ ZrO_2 were abbreviated as Z, A, 10ZA, 20ZA, 40ZA and MZ respectively.

2.5 Characterization of solid acids

The solid acids such as Z, A, ZA and MZ were analyzed for their surface acidity by $\text{NH}_3\text{-TPD}$ (Mayura TPD unit), crystallinity by Powder X-ray diffraction (Philips X'Pert diffractometer using $\text{CuK}\alpha$), functionality by FT-IR (Nicolet) technique, morphology by TEM (JEOL 2010) and ICP-OES (i-CAP 6000) method was used for elemental analysis.

2.6 Catalytic activity of solid acids (in the microwave irradiated synthesis of biphenyl urea)

Biphenyl urea (Scheme 1) was synthesized by taking a mixture of aniline (10 mmol), dimethyl carbonate (20 mmol) and 0.1 g of the solid acid catalyst (Z or A or ZA or MZ) in a microwave reactor vessel. The total volume of the reaction mixture was maintained always at 20 mL. The reaction mixture was heated in a microwave reactor (Labmatrix India Pvt Ltd) fitted with a reflux condenser at 383 K for a fixed period of time with stirring. The maximum irradiation power of 1100 W was used in the initial 1.0 min of the reaction to obtain the desired reaction temperature, and then, variable power of 500–650 W was used. After the stipulated reaction time the reactor vessel was taken out from the microwave reactor and cooled to room temperature

Scheme 1 Synthesis of BPU from aniline and dimethyl carbonate over a solid acid catalyst

to which 10 mL of hot ethanol was added to dissolve the solid product. The solid acid catalyst was separated from the reaction mixture by filtration. The organic layer left behind was kept aside for crystallization of biphenyl urea (BPU). The product consisting of BPU was analyzed for its melting point (Anamatrix), ^1H NMR spectroscopy (Bruker, 400 MHz) and LC–MS (Varian).

Further, reactions were carried out to optimize the conditions like nature of the solid acid catalyst, weight of catalyst, reaction temperature and reaction time.

The kinetic studies were conducted in a temperature range from 353 K to 393 K. The reactions were carried out by following the procedure as mentioned in the earlier paragraph, by varying the amount of catalysts (0.05–0.2 g) and reaction time (2.0–20.0 min).

The conversion (%), selectivity (%) and yield (%) of products was calculated by using the following equations:

$$\text{Conversion (\% aniline)} = 100 - 100 \times \frac{[\text{Aniline}]}{[\text{Aniline} + \text{DMC}]}$$

$$\text{Selectivity (\% BPU)} = 100 \times \frac{[\text{BPU}]}{[\text{BPU}] + [\text{N-methylaniline}]}$$

$$\text{Yield (\% BPU)} = 100 \times \frac{\text{Experimental yield of BPU}}{\text{Theoretical yield of BPU}}$$

2.7 Reactivation and reusability of solid acids

The used solid acid was washed thoroughly with acetone, dried in an oven and finally calcined for 1 h at 823 K. Such reactivated solid acid was reused in the next consecutive cycle of BPU synthesis.

3 Results and discussion

3.1 Acidity of the solid acids

The data pertaining to the total surface acidity (TSA) and acid site distribution of solid acid catalysts determined by NH_3 -TPD method are shown in Table 1.

Pure oxides such as zirconia and alumina were least acidic compared to their mixed oxide forms. However, mixed oxides were found to be more acidic than their individual forms. Increase in the acidity of mixed oxides can be due to the imbalance of positive charge when Al^{3+} is inserted into Zr^{4+} lattice, which creates Lewis acid sites [20]. Interestingly, all the solids used for the present work consisted of only 'weak and moderate' acid sites. MZ samples consisted of 'moderate and strong' sites [6].

Table 1 Acidic properties of solid acids used for the present work

Solid acid	Acid site distribution (mmol/g)			TSA (mmol/g)
	Weak	Moderate	Strong	
Z	0.04	0.35	–	0.39
A	0.08	0.36	–	0.44
10AZ	0.13	0.55	–	0.68
20AZ	0.19	0.80	–	0.99
40AZ	0.23	0.95	–	1.18
MZ	–	0.99	0.24	1.23

3.2 PXRD of solid acids

The powder XRD patterns of Z, A, ZA and MZ samples are presented in Fig. 1[A]. PXRD patterns of Z and A shows the characteristic reflections pertaining to monoclinic, tetragonal and rhombohedral phases respectively. Whereas, in case of ZA, reflections due to a mixture of tetragonal and rhombohedral phases could be seen. No reflections pertaining to monoclinic phase of zirconia were observed in ZA samples. When the PXRD patterns of 10ZA, 20ZA and 40 ZA samples are observed, the intensity of peaks corresponding to tetragonal phase of zirconia increases gradually with an increase in the concentration of zirconia [21]. This is due to a relative decrease in the concentration of Al_2O_3 as well as due to inherently poor intensity of peaks related to Al_2O_3 . In case of 40ZA, no peaks corresponding to alumina are observed. i.e., peaks due to tetragonal zirconia are seen. This indicates that 40ZA consists of only tetragonal phase which is catalytically active. Interestingly no peaks corresponding to monoclinic ZrO_2 are observed in the PXRD patterns of ZA samples. PXRD pattern of MZ consisted of only tetragonal phase of zirconia and monoclinic phase is absent indicating the phase stabilization property of Mo(VI) ions (Fig. 1[B]).

Further, a correlation between the surface acidity, tetragonal phase and the catalytic activity of zirconia based solid acids could be observed. The solid acid 40AZ which contains tetragonal phase was found to be more acidic and more catalytically active in the acid catalyzed reaction between aniline and DMC leading to the formation BPU.

3.3 FT-IR studies of solid acids

Figure 2 represents FT-IR spectra of Z, A and ZA. The presence of Zr–OH (bending mode) and Zr–O–Zr (stretching mode) are indicated by the bands at $\sim 1391\text{ cm}^{-1}$ and $\sim 1118\text{ cm}^{-1}$ respectively which indicate the presence of ZrO_2 phases in all the solid acids used for the present work except for alumina. A broad band at $\sim 1600\text{ cm}^{-1}$ due to the vibrations of acidic –OH and another band

Fig. 1 [A] PXRD patterns of solid acids: **a** Al_2O_3 , **b** ZrO_2 , **c** 10AZ **d** 20AZ and **e** 40AZ. [R-rhombohedral Al_2O_3 , T-tetragonal ZrO_2]. [B] PXRD pattern and FTIR spectra of MZ sample

Fig. 2 FTIR spectra of solid acids: **a** Al_2O_3 , **b** ZrO_2 , **c** 10AZ **d** 20AZ and **e** 40AZ

at $\sim 3400\text{ cm}^{-1}$ (stretching mode) with hydrogen bonding can also be observed. For the samples containing alumina, bands at 1050 cm^{-1} , 770 cm^{-1} and 690 cm^{-1} corresponding to O–Al vibrations could be seen [4].

3.4 TEM studies

TEM image of $40\text{ZrO}_2\text{-Al}_2\text{O}_3$ is shown in Fig. 3. The particle size of 40AZ was found to be in the range between 25–40 nm indicating that it is *mesoporous* in nature.

Fig. 3 TEM image of 40AZ

3.5 ICP-OES studies

The elemental analysis carried out for ZA solid acids via ICP-OES indicates the presence of 10.2%, 20.6% and 40.9% of zirconia in 10ZA, 20ZA and 40ZA samples respectively. MZ sample consisted of 4.8% Mo(VI).

3.6 Catalytic activity studies of solid acids (in microwave-assisted BPU synthesis)

The microwave-assisted reactions between aniline and DMC were carried out over the solid acids (Z, A, ZA, MZ) used for the present study (Table 2). A correlation

Table 2 Comparative catalytic activity of Z, A, ZA and MZ in microwave-assisted BPU synthesis

Solid acid	Conversion of aniline (%)	Selectivity towards BPU (%)	Selectivity towards by-products (%)
Z	46	100	00
A	49	100	00
10ZA	61	100	00
20ZA	77	100	00
40ZA	98	100	00
MZ	100	77	23

[Reaction conditions Molar ratio of aniline: DMC = 1: 3, weight of solid acid = 0.1 g, temperature = 383 K, time = 12 min]

between the acidic properties and the catalytic activity was observed. Zirconia and alumina having lowest acidity showed least activity in the reaction followed by other solid acids such as MZ and ZA. Among ZA samples, 40ZA showed highest conversion of aniline when compared to either 10ZA or 20ZA which can be due to its highest acidity and possess catalytically active tetragonal phase of zirconia. Further, it is reported that rhombohedral alumina is less active in acid catalysed reactions [22]. Hence, 10ZA and 20ZA consisting of rhombohedral alumina are less active when compared to 40ZA.

However, over MZ in addition to BPU and N-methyl aniline was also formed as the by-product. The formation of by-product can be attributed to the presence of 'strong' acid sites in MZ. This infers that the formation of BPU requires 'weak and moderate' sites. Even though MZ shows 100% conversion of aniline, it is less selective towards the formation of BPU (1,3-biphenyl urea). Therefore, for further optimization work, 40ZA was chosen because it produced reasonably good yield of BPU (98%) with 100% selectivity.

3.7 Effect of mole ratio of the reactants on the conversion (%) of aniline

The reactions were conducted with molar ratios of aniline: DMC = 1:1, 1:2, 1:3, 1:4 and 1:5 in presence of 0.05 g of 40ZA solid acid under microwave irradiation and the results are presented as Fig. 4. With an increase in the molar ratio of the reactants, the conversion (%) of aniline also increased from 42 to 98. This is because the reaction between aniline with DMC is an equilibrium chemical reaction and since the position of equilibrium controls the amount of BPU formed, the use of an excess of DMC increases the conversion (%) of aniline. However, the increase in the conversion was up to a molar ratio of 1:3 but becomes almost stable beyond this molar ratio. Therefore, for further optimization studies molar ratio of aniline: DMC = 1:3 was found to be suitable.

Fig. 4 Effect of molar ratio of aniline: DMC on the conversion (%) of aniline. [Reaction conditions Amount of 40ZA solid acid = 0.1 g, temperature = 383 K, time = 12 min]

3.8 Effect of reaction time on the conversion (%) of aniline

The reactions between aniline and DMC were conducted at different reaction times ranging from 2 min to 20 min and the results are presented in Fig. 5. The conversion (%) of aniline increased with an increase in the reaction time until 12 min and reached 98%. Further increase in the reaction time beyond 12 min did not show any reasonable change in the conversion (%) of aniline indicating that the reaction attains equilibrium when the reaction

Fig. 5 Effect of reaction time period on the conversion (%) of aniline. [Reaction conditions Molar ratio of aniline: DMC = 1: 3, weight of 40ZA solid acid = 0.1 g, temperature = 383 K]

time reaches 12 min. Therefore, 12 min was selected as the optimum reaction time.

3.9 Effect of reaction temperature on the conversion (%) of aniline

The reaction temperature was varied in the range from 353 K to 393 K and its effect on the conversion of aniline over 40ZA solid acid and the results are given Fig. 6. The conversion (%) of aniline was found to get increased with an increase in the temperature (up to 383 K) because increasing the temperature apparently favors the acceleration of the forward reaction. Beyond 383 K, though the conversion of aniline increased slightly, the selectivity towards the desired product BPU was found to decrease with the formation of the expected by-product such as N-methyl aniline. This indicates that the formation of by-product is not only influenced by the presence of strong acid sites on the catalyst (MZ catalyst) but also influenced by elevated reaction temperature which involves higher energy. Therefore, 383 K was chosen as the optimum reaction temperature for the synthesis of BPU with 100% selectivity over 40ZA solid acid.

3.10 Effect of amount of the catalyst on the conversion (%) of aniline

The effect of amount of solid acid catalyst on the conversion (%) of aniline was studied by varying the catalyst weight from 0.05 to 0.2 g (Fig. 7). An increase in the amount of the catalyst resulted in an increase the conversion (%) of aniline till 0.01 g. Further increase in the

Fig. 6 Effect of reaction temperature on the conversion (%) of aniline. [Reaction conditions Molar ratio of aniline: DMC = 1: 3, weight of 40ZA solid acid = 0.1 g, time = 12 min]

Fig. 7 Effect of amount of the solid acid catalyst on the conversion (%) of aniline. [Reaction conditions Molar ratio of aniline: DMC = 1: 3, temperature = 383 K, time = 12 min]

amount of the catalyst did not show significant increase in the conversion (%) of aniline.

3.11 Effect of heating method (microwave v/s conventional heating)

The reactions between aniline and DMC were carried out by using two different heating methods such as microwave heating and conventional heating. The reactions were carried out over 40ZA solid acid under a set of reaction conditions and the results are shown in Table 3. The results clearly indicate that the microwave heating method is faster and facile when compared to conventional heating method.

In case of conventional heating, the reaction proceeded exceptionally slow since first heat is imparted to the reactants by transferring through the walls of the reaction vessel by making it a very slow as well as an inefficient method regarding transportation of energy into the reacting system is concerned. But, microwave heating was found to be superior with highest conversion (%) of aniline (~ twofold) in 12 min as compared to conventional

Table 3 Comparison between methods of heating with respect to the conversion (%) of aniline

Heating method	Reaction time (min)	Conversion of aniline (%)
Microwave	12	98
Conventional	12	41
Conventional	80	84

method. Further, up to 84% conversion of aniline was obtained when the reactions were carried out for 100 min under conventional heating method. Besides, the application of microwave energy is an expressway with higher reaction rates, reduced reaction times in managing and initiating the reaction towards equilibrium compared to conventional thermal radiation [14].

3.12 Synthesis of various BPU derivatives over 40ZA

The activity of 40ZA which showed excellent activity in the synthesis of BPU was further evaluated in the synthesis of BPU derivatives. The reactions were carried out with substituted anilines with DMC at 383 K for 12 min. The yield (%) of the BPU products are recorded in the Table 4 and the spectral data of the obtained BPU derivatives are given in the Table 5. When secondary substituted anilines were used in the reaction, the conversion of aniline is very low.

Whereas primary substituted anilines, when employed in a reaction, up to 90% yield of desired BPU derivatives was obtained.

3.13 Kinetic studies

The kinetic studies were conducted to compare the catalytic activity of heterogeneous solid acids (40AZ and MZ). Proceeding towards kinetic examination, experiments were performed to establish the mass and heat transfer limitations. Experiments were also conducted with different stirring rates for the reaction mixture. It was observed that the conversion (%) aniline was independent of stirring rates. Not much change the conversion (%) aniline was noticed. It may be assumed that any external resistance to its transfer from bulk liquid phase to the external surface is absent [23].

Table 4 Microwave irradiated synthesis of BPU derivatives over 40ZA

Entry No.	Aniline	Product	Yield (%)
1			98
2			98
3			68
4			35
5			93

[Reaction conditions: Molar ratio of aniline: DMC = 1: 3, weight of solid acid = 0.1 g of 40ZA, temperature = 383 K, time = 12 min].

[Reaction conditions: Molar ratio of aniline: DMC = 1: 3, weight of solid acid = 0.1 g of 40ZA, temperature = 383 K, time = 12 min]

Table 5 Spectral data of BPU derivatives (Refer to Table 4)

Entry No.	Product	Spectral data
1	1,3-biphenyl urea	White crystalline shiny solid, M.P 239–241 °C, IR (KBr) 3291 cm ⁻¹ (N–H), 1635 cm ⁻¹ (C=O). ¹ HNMR (300 Hz, DMSO), ¹ H: 6.52–7.4 (Ar–H, m, 10H), 8.2 (N–H, s, 2H). Ms: M ⁺ =213.2.
2	1,3-dio-tolyl urea	Pale yellow crystalline solid, M.P 283–285 °C, IR (KBr) 3307 cm ⁻¹ (N–H), 2935 cm ⁻¹ (C–H) 1641 cm ⁻¹ (C=O). ¹ HNMR (300 Hz, DMSO), ¹ H: 6.92–7.79 (Ar–H, m, 8H), 8.24 (N–H, s, 2H), 2.50 (–CH ₃ , s, 3H). Ms: M ⁺ =241.
3	1,3-bis(2-amino phenyl) urea	Yellow crystalline compound, IR (KBr) 3291 cm ⁻¹ (N–H), 3347 cm ⁻¹ and 3169 cm ⁻¹ (–NH ₂), 1629 cm ⁻¹ (C=O). ¹ HNMR (300 Hz, DMSO), ¹ H: 6.72–7.34 (Ar–H, m, 8H), 8.34 (N–H, s, 2H). Ms: M ⁺ =241.
4	1,3-bis(2-nitrophenyl) urea	Yellow crystalline solid; M.P=235–237 °C, IR (KBr) 3347 cm ⁻¹ (N–H), 1328 cm ⁻¹ (N=O) 1649 cm ⁻¹ (C=O). ¹ HNMR (300 Hz, DMSO), ¹ H: 6.92–7.59 (Ar–H, m, 8H), 8.54 (N–H, s, 2H). Ms: M ⁺ =303.2.
5	1,3-bis(4-chloro phenyl) urea	White crystalline shiny solid; M.P=> 300 °C, IR (KBr) 3297 cm ⁻¹ (N–H), 1637 cm ⁻¹ (C=O), 877 cm ⁻¹ (C–Cl). ¹ HNMR (300 Hz, DMSO), ¹ H: 7.32–7.51 (Ar–H, m, 8H), 8.85 (N–H, s, 2H). Ms: M ⁺ =283.

Graphs of $-\ln[1-\text{Yield of BPU}]$ against reaction time discussed at different temperatures over 40ZA and MZ catalysts and presented in Fig. 8. Order of reaction was found to be first-order because linearity was noticed among all the plots.

The first-order rate constants obtained from the slopes and activation energy (E_a) determined using Arrhenius equation is given in Table 6.

$$E_a = 2.303R \log \left(\frac{k_2}{k_1} \right) \left[\frac{T_1 \times T_2}{T_2 - T_1} \right]$$

where R =gas constant, k_1 =rate constant at temperature T_1 and k_2 =rate constant at temperature T_2 .

In this work, faster kinetics was noticed in the case of 40ZA catalyst with a shorter reaction time 12 min when compared to a solid super acid (MZ) towards the formation of the desired reaction product i.e., BPU. This suggests that 40ZA is a proficient-solid acid for the present work.

3.14 Reusability of solid acids

Reusability studies of solid acid catalysts such as 40ZA and MZ was investigated in microwave-assisted reaction between aniline and DMC in a molar ratio of 1:3 at 383 K for 12 min. After the first reaction cycle, the solid product was separated from the mixture by adding 10 ml of hot ethanol followed by filtration. The used solid acid catalyst was washed with acetone to remove any adsorbed organic impurities from the surface of the catalyst, dried in an air oven at 493 K for 2 h and calcined at 823 K for 1 h. Thus reactivated catalysts were reused in the next consecutive reaction cycle and six such reusability cycles were studied and the data are presented in the form of Fig. 9.

It was observed that 40ZA solid acid was more reusable with no significant loss in its catalytic activity. However, MZ solid acid was found to deactivate gradually during its

Fig. 8 The plot of first order rate constants for the reaction between aniline and DMC in the presence of 40ZA and MZ catalysts at 363 K, 373 K and 383 K

Table 6 The energy of activation (E_a) & rate constants (k) of 40ZA and MZ solid acid catalysts on yield (%) of BPU

Solid acid catalyst	Rate constant $\times 10^{-3} \text{ min}^{-1}$ (Yield of BPU)		E_a for the Yield of BPU (kJ/mol)
	373 K	383 K	
40ZA	1.36	2.29	42.0
MZ	1.22	2.89	66.2

Fig. 9 Effect of reactivation of solid acid catalysts (40ZA and MZ) on the conversion (%) of aniline

reuse in the consecutive reaction cycles which can be due to the strong adsorption of reactant or product molecules on the strong acid sites of MZ.

4 Conclusions

Selective and fast synthesis of biphenyl urea was successfully carried out over zirconia-alumina based solid acids under microwave irradiation in a shorter period of time of just 12 min. A correlation between the acidity of solid acid and the conversion of aniline was observed. The selectivity of BPU was influenced by the acid site distribution of solid acid catalyst. Zirconia-alumina which consisted of weak and moderate acid sites produced biphenyl urea with 100% selectivity. But Mo(VI)/ZrO_2 was found to be less selective towards the formation of BPU because it also produced N-methyl aniline as the by-product as it has 'strong' acid sites. $\text{ZrO}_2\text{-Al}_2\text{O}_3$, especially mesoporous $40\text{ZrO}_2\text{-Al}_2\text{O}_3$ was ecofriendly and can be recycled for at least 6 reaction cycles without much deactivation. This solid acid can be successfully used as catalyst for the synthesis of BPU derivatives. Kinetic studies indicate that $40\text{ZrO}_2\text{-Al}_2\text{O}_3$ is

more efficient with low E_a in the selective synthesis of biphenyl urea.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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