Effective synthesis of quinoxalines over ceria based solid acids coated on honeycomb monoliths

Venkatesh a,b, S Z Mohamed Shamshuddin a,b, & N M Mubarak c

aChemistry Research Laboratory, HMS Institute of Technology, NH4, Kyathsandra, Tumkur, Karnataka, India
bResearch and Development Center, Bharathiar University, Coimbatore, India
cDepartment of Chemical Engineering, University of Malaya, Kuala Lumpur, Malaysia

Email: mohamed.shamshuddin@gmail.com

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Solid acids of ceria such as sulfated ceria, ceria-zirconia mixed oxide and sulfated ceria-zirconia have been coated on honeycomb monoliths by slurry coating method. The catalyst materials are characterized by NH₃-TPD for surface acidity, powder XRD for crystallinity and SEM for morphology. These materials are used as solid acid catalysts in the condensation reaction of various diamines and diketones to synthesize quinoxalines. In order to optimize the reaction conditions, the effect of reaction parameters such as the catalyst type, nature of the solvent, reaction temperature, nature of the catalyst and number of reaction cycles on the yield of the quinoxaline product has been studied. A correlation between the surface acidity and the catalytic activity is observed. The catalyst materials have also been prepared in their powder forms by impregnation method and their catalytic activity is compared with that of their honeycomb coated forms. The ceria based solid acids coated on honeycomb monoliths are economical, efficient and eco-friendly in quinoxaline synthesis.

**Keywords:** Catalysts, Solid acids, Quinoxalines, Honeycomb monoliths, Ceria, Sulfated ceria, Ceria-zirconia, Zirconia

Quinoxalines are a class of benzo-heterocycles having a wide range of biological activities, which have made them important as pharmacologically active compounds. Quinoxalines also play a vital role in the synthesis of many insecticides, fungicides, herbicides, antibiotics, etc. Generally, quinoxalines are synthesized by the condensation of various diamines and diketones to synthesize quinoxalines. In order to optimize the reaction conditions, the effect of reaction parameters such as the catalyst type, nature of the solvent, reaction temperature, nature of the catalyst and number of reaction cycles on the yield of the quinoxaline product has been studied. A correlation between the surface acidity and the catalytic activity is observed. The catalyst materials have also been prepared in their powder forms by impregnation method and their catalytic activity is compared with that of their honeycomb coated forms. The ceria based solid acids coated on honeycomb monoliths are economical, efficient and eco-friendly in quinoxaline synthesis.

**Keywords:** Catalysts, Solid acids, Quinoxalines, Honeycomb monoliths, Ceria, Sulfated ceria, Ceria-zirconia, Zirconia

Cordierite (Mg₂Al₄Si₅O₁₈) honeycomb monolith plays a vital role as catalyst carrier for heterogeneous catalysts. Monolith supports are uni-body structures composed of interconnected repeating cells or channels. Catalysts (ceria based composites; Ceₓ₋ₓMₓO₂₋ₓ) coated with honeycomb monoliths are widely used in automotive applications which involve gas phase reactions such as combustion of volatile organic compounds, automotive applications, ozone abatement in aircrafts and selective reduction of NOₓ, etc. Catalysts coated on HC monoliths have advantages over powder catalysts due to high active surface area. A small amount of the catalyst loaded on the monoliths is highly effective and gives easy separation and complete recovery of the catalysts from the reaction mixture. The use of honeycomb monoliths as carriers especially for solid catalysts would be a very cost effective and eco-friendly process and will also be an interesting initiative step in the field of liquid phase organic synthesis.
Keeping in view the industrial importance of quinoxalines and ceria based solid acid catalysts coated on honeycomb (HC) carriers, in the present article the synthesis of quinoxalines over solid acids such as CeO₂, SO₄²⁻/CeO₂, CeO₂-ZrO₂ and SO₄²⁻/CeO₂-ZrO₂ coated on HCs is reported. The solid acids were coated on HCs by slurry coating method and characterized for their surface acidity by NH₃-TPD, crystallinity by PXRD and morphology by SEM techniques. Quinoxalines were synthesized by the condensation of various 1,2-dimaines and 1,2-ketones over these solid acids. The ceria based solid acids were also synthesized in their powder forms and their catalytic activity has been compared with that of their HC coated forms. In order to obtain the highest possible yield of the quinoxaline product, the reaction conditions were optimized by varying the catalyst type, the solvent, reaction temperature and nature of the catalyst. The effect of reactivation and reusability of ceria solid acid on the yield of quinoxaline derivatives was also investigated.

Materials and Methods

Cordierite honeycomb monoliths having dimensions (height = 1.20 cm, diameter = 2.50 cm and hole = 0.2 cm) were supplied by Shreya ceramics, Baroda, India. Ceric ammonium nitrate, zirconyl nitrate and sulfuric acid were supplied by Loba Chemie India Ltd., India. Diamines and diketones were from either Merck or Sigma Aldrich India Limited.

Preparation and characterisation of catalytic materials

The HCs were wash-coated with metal oxides such as alumina or zirconia before coating the active catalysts. It was reported that before coating an active catalyst, if the bare honeycomb is wash coated with simple metal oxides such as alumina or zirconia, the active catalyst can form an adherent coating on the honeycomb surface. Wash coating with zirconia was preferred as it increases the surface area and gives the HC support material a better interaction with the active catalysts when compared to other metal oxides. For wash coating with zirconia on a bare HC, 1.5 g of zirconyl nitrate was dissolved in 50 mL of deionized water. The resulting solution was coated on a HC by dipping and drying in a furnace preheated to 400 °C 10-12 times till ~0.02 g of zirconia was coated on the HC.

Preparation of ceria (CeO₂) and ceria-zirconia (CeO₂-ZrO₂) mixed oxides

Known amounts of ceric ammonium nitrate and deionised water were taken in a beaker and this solution was coated on a wash coated HC by the dipping and drying process using a muffle furnace maintained at 400 °C. Dipping and drying steps were carried out 5-7 times such that ~0.05 g of the active catalyst was coated on the honeycomb. A higher amount of catalyst cannot be coated on a honeycomb since it may lead to the formation of multilayer catalyst coating. Further, due to increase in the thickness of the inner walls of the HC, the reactant molecules may be blocked from entering into the holes of the HC. A lower amount is compensated by its higher efficiency due to good mass-transfer characteristics.

Ceria-zirconia mixed oxide was prepared in a similar way by using ceric ammonium nitrate and zirconyl nitrate.

Preparation of (SO₄²⁻/CeO₂) and (SO₄²⁻/CeO₂-ZrO₂)

A known amount of previously prepared hydrated ceria (3.0 g) was taken in a beaker to which 6 M H₂SO₄ (2 mL) was added and the resulting mixture was made into a fine slurry. The slurry was then coated on a wash coated HC by dipping and drying method by using a muffle furnace maintained at 400 °C.

Sulfated ceria-zirconia was prepared in a similar way by using previously prepared ceria-zirconia (3.0 g) mixed oxide and 6 M H₂SO₄ (2 mL). All the catalytic materials were also prepared in their powder forms by impregnation method. The catalytic materials (both HC coated and powder forms) were calcined at 550 °C for 5 h before their use as solid acid catalysts. The catalytic materials are abbreviated as CeO₂ (C), CeO₂-ZrO₂ (CZ), SO₄²⁻/CeO₂ (SC) and SO₄²⁻/CeO₂-ZrO₂ (SCZ).

The catalytic materials (both HC coated and powder forms) were characterized by NH₃-TPD method for the measurement of surface acidity. Powder XRD (PXRD) patterns were recorded on a X-ray diffractometer (Philips X’pert) using CuKα (λ = 1.5418 Å) and SEM images were recorded on JEOL-2010.

Catalytic activity

All the solid acids were evaluated for their catalytic activity in the condensation reaction of 1,2-diamine, 1,2-diketone in presence of a suitable solvent (Scheme 1).

In a typical reaction, a mixture of 1,2-diamine, 1,2-diketone in 1:1 molar ratio, solvent (20 mL) and 0.05 g of the solid acid catalyst (either in HC coated or powder form) was taken in a 50 mL specially
designed reactor and heated over magnetic stirrer at ~45 °C. After a stipulated time, the reaction mixture was cooled and mixed with 10 mL of ethanol and filtered to separate the solid acid catalyst. The filtrate was rota-vapourised to remove the solvents and the solid product was recrystallized from ethanol.

The product analysis was carried out by measuring their melting point and by NMR spectroscopic methods. The melting point of the isolated products was recorded in an open capillary tube. 1H NMR and 13CNMR spectra were obtained at 400 MHz NMR spectrometer (Bruker).

Results and Discussion

Characterization of catalytic materials

Total surface acidity (TSA)

The TSA values of solid acid catalytic materials (HC coated form) used in the present study are given in Table 1. TSA values were found to follow the order: SCZ > SC > CZ > Z > C. Among the solid acids, pure ceria was found to be least acidic when compared to its modified forms. It has been reported that the incorporation of ceria into zirconia or vice-versa increases the acidity of the resulting mixed oxide (i.e., CeO2-ZrO2) to a reasonable extent. A similar observation has been reported by Pengpaniche et al.21 and Reddy et al.22 A possible explanation for the enhancing acidity may be as follows: The incorporation of zirconium cation into the ceria unit cell or vice versa modifies the surface acid-base sites, as the exposed Ce4+ and Zr4+ ions act as Lewis acid sites. Both CeO2 and ZrO2 exhibit the same metal-oxygen stoichiometry but possess different ionic characters. Ceria is considered to be more ionic than zirconia. The acid strength of the mixed oxide varies depending on the charge-to-radius ratio of the cation as well. The Zr4+ ion has an ionic radius of 0.84 Å which is smaller than that of Ce3+ (0.97 Å) and is expected to generate a larger number of acid sites in their mixed form.

Further, it is well cited in the literature that the sulfation of pure metal oxides increases the acidity to a certain extent23. A similar finding has been observed in the present study, i.e., both SC and SCZ were found to be highly acidic when compared to their pure forms. An increase in the surface acidity in the case of SCZ, may be due to the existence of different types of sulphate phases such as CeOSO4 and Zr(SO4)2 as reported by Putlasudarshan et al.24 Further, it was observed that pure ceria or pure zirconia consisted of only ‘weak’ and ‘moderate’ acid sites. Whereas, CZ consisted of mostly ‘moderate’ acid sites and SC or SCZ consisted of ‘moderate’ as well as ‘strong’ acid sites.

Table 1—Acid site distribution and TSA values of solid acid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid site distribution (mmol/g)</th>
<th>TSA (mmols/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak Moderate Strong</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.11 0.18 0.00</td>
<td>0.29</td>
</tr>
<tr>
<td>Z</td>
<td>0.13 0.21 0.00</td>
<td>0.34</td>
</tr>
<tr>
<td>CZ</td>
<td>0.13 0.56 0.02</td>
<td>0.71</td>
</tr>
<tr>
<td>SC</td>
<td>0.14 0.37 0.22</td>
<td>0.73</td>
</tr>
<tr>
<td>SCZ</td>
<td>0.11 0.39 0.29</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Powder X-ray diffraction (PXRD)

PXRD patterns of solid acids (C, CZ, SC, SCZ) coated on HC monoliths are given in Fig. 1. Pure ceria shows the characteristic reflection at 2θ (deg.) = 28.5, 33.4, 47.3, 56.2, which corresponds to the fluorite structure of ceria.25 In the case of CZ mixed oxide, reflections due to both fluorite structure of ceria and reflections due to tetragonal phase of zirconia (2θ (deg.) = 30.2, 35.1, 50.4, 60.0) could be observed.26 However, reflections due to the monoclinic phase of zirconia were absent. This indicates the structure stabilizing property of ceria on zirconia wherein the tetragonal phase of zirconia is stabilized by ceria.

As can be seen in the Fig. 1, the PXRD pattern of CZ and SCZ differ very much indicating a strong influence of sulfate ions on ceria-zirconia mixed
oxide. In the case of SCZ, in addition to reflections due to fluorite structure of ceria and tetragonal phase of zirconia, reflections due to different types of surface zirconium sulfates such as zirconium sulfate hydroxide \([\text{Zr(OH)}_2\text{SO}_4]\) and zircosulfate \([\text{Zr(SO}_4)_2]\) were observed\(^{22}\). No reflections pertaining to cerium sulphate or bare HC were seen. The PXRD patterns of solid acids in their HC coated forms as well as in their powder forms were found to be similar.

**Scanning electron microscopy (SEM)**

SEM images of HCs coated with solid acids as well as bare HC (uncoated) are shown in Fig. 2. These images show the strong adherence of the active catalyst on the surface of the HC. Also, the coating of the catalyst is considerably uniform. This information obtained from SEM also indicates that the method used for coating the catalytic material was suitable to obtain adherent and homogeneous coating of the catalytic material. In the case of the SEM images of either C or CZ or SCZ, no distinguishable features could be observed, which indicates the formation of a homogenous solid solution between ceria and zirconia.

**Catalytic activity**

Synthesis of quinoxalines was carried out to evaluate the activity of the catalytic materials (Scheme 1). To begin with, the condensation reaction between the diamine (o-phenylene diamine; OPDA) and diketone (diphenyl ketone; DPK) was carried out in the absence of any catalyst and no product was observed up to 4 h. However, about 12% of product was observed after refluxing the reaction mixture for 24 h.

When the reactions were carried out in presence of solid acid catalysts (C, CZ, SC, SCZ), the expected quinoxaline product (2,3-diphenylquinoxaline) was obtained in higher yield in shorter reaction period. This study indicates that the condensation reaction between a diamine and a diketone is a catalytic reaction.

![Fig. 2—SEM images of HCs coated with (a) bare HC, (b) C, (c) CZ and (d) SCZ. (Magnification = 2000x; 10 µm).](image)

![Scheme 1](image)
Effect of catalyst

Quinoxaline synthesis was carried out over OPDA and DPK in presence of EtOH-water (3:2) over different HC catalysts and the results are given in Table 2. The catalytic activity of the solid acid catalysts used for the present work followed the order similar to the order of their TSA, i.e., SCZ > SC > CZ > Z > C. This indicates that the TSA values of the solid acid catalyst and yield (%) of quinoxaline derivative (2,3-diphenylquinoxaline) are co-relative. In the case of sulphated oxides such as SC and SCZ, the yield of the desired quinoxaline product is 94% and 98% respectively, which is higher than the yield of quinoxaline product over CZ catalyst (i.e., 89%). However, the selectivity of the desired product (quinoxaline) depends on the strength of the acid sites on the catalyst material. It has been reported that the formation of a quinoxaline product required ‘moderate’ acid sites. The same results are reflected in the present study. Since sulphated catalysts consist of both ‘moderate’ and ‘strong’ acid sites, in addition to the desired quinoxaline product by-products were also formed to an extent of 2–6%. Formation of by-products other than quinoxaline can be attributed to the presence of ‘strong’ acid sites in sulphated ceria and sulphated-ceria-zirconia. Moreover, the color of the catalyst as well as the color of the reaction mixture turned grayish during the course of the reaction over SC or SCZ. The formation of by-products may be due to the decomposition of either the reactants or reactive intermediates or the products in to by-products by side reaction. Therefore, sulphated oxides such as sulphated ceria and sulphated-ceria-zirconia were less selective towards the formation of the desired quinoxaline product when compared to non-sulphated oxides such as zirconia, ceria, ceria-zirconia which are 100% selective towards the formation of desired quinoxaline products. Even though pure C and Z solid acids were 100% selective towards the formation of quinoxalines, the yield of quinoxalines was very poor as they consisted of very few ‘moderate’ acid sites.

Over CZ catalyst no by-products were formed and no discoloration of the catalyst was observed. This can be attributed to the absence of ‘strong acid’ sites. Since CZ consists of a reasonably high number of ‘moderate’ acid sites, it showed good activity in quinoxaline synthesis with 100% selectivity. Hence, CZ was selected as the solid acid catalyst for further optimization studies.

Effect of solvent

In order to study the effect of solvent on the yield of quinoxalines, the reactions were carried out with OPDA and DPK in presence of polar-protic solvents such as methanol, ethanol, n-propanol and mixed solvents such as ethanol-water, methanol-water and n-propanol-water over HC coated with CZ catalyst. It has been reported that the yield of quinoxaline (2,3-diphenylquinoxaline) could be higher in presence of polar-protic solvents when compared to polar-aprotic or non-polar solvents. The yield of quinoxalines over the solvents such as methanol, ethanol, n-propanol, water, and mixed solvents such as methanol-water, ethanol-water and n-propanol-water were 64%, 65%, 69%, 71%, 75%, 88% and 72% respectively. The yield of quinoxaline was highest (88%) when ethanol-water was used as a solvent.

Further, the reactions were carried out by varying the ratio of ethanol to water. The order of yield was found to be (i.e., EtOH:water = 1:4, (72%) 2:3, (76%) 1:1, (80%) 3:2, (89%) and 4:1 (91%)). The highest yield (%) of quinoxaline was obtained with the EtOH:water ratio of 3:2. However, not much increase in the yield of quinoxalines was observed when the concentration of EtOH in EtOH:water mixture was increased beyond 3:2. Therefore, the solvent mixture comprising of EtOH:water in the ratio 3:2 was found to be suitable for obtaining highest yield of quinoxaline.

Effect of reaction temperature

The condensation reaction between OPDA and DPK was carried out over HC coated with CZ catalyst in presence of EtOH:water (3:2) solvent mixture in the reaction temperature ranging from 25 °C to 60 °C. Although the formation of quinoxaline product began at room temperature, the yield (%) of the

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**Table 2—Yield (%) and selectivity (%) of quinoxaline derivative over different catalyst materials used in the present study.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield of 2,3-diphenylquinoxaline (%)</th>
<th>Selectivity of quinoxaline (%)</th>
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<tbody>
<tr>
<td></td>
<td>HC coated</td>
<td>Powder form</td>
</tr>
<tr>
<td>C</td>
<td>41</td>
<td>29</td>
</tr>
<tr>
<td>Z</td>
<td>48</td>
<td>30</td>
</tr>
<tr>
<td>CZ</td>
<td>89</td>
<td>45</td>
</tr>
<tr>
<td>SC</td>
<td>94</td>
<td>51</td>
</tr>
<tr>
<td>SCZ</td>
<td>98</td>
<td>57</td>
</tr>
</tbody>
</table>
quinoxaline was found to increase with the reaction temperature. The maximum yield of quinoxaline was observed when the temperature was increased from 30 °C to 40 °C (there was 30% increase in the yield from 69% to 89%). However, when the temperature was increased from either 40 °C to 50 °C or 50 °C to 60 °C, the increase in the yield was only 9% (from 89% to 98%).

**Comparative catalytic activity of HC coated and powder forms**

The catalytic activity of solid acids in their HC coated forms and powder forms were compared in the synthesis of quinoxalines (OPDA+DPK) (Table 2). When the activity of these two types of catalysts was observed, the solid acid catalysts coated on HCs were found to be more efficient when compared to their powder form.

Even though the same amount of solid acid catalyst (~0.05 g) was used either in its HC coated form or in its powder form, approximately 1.7 fold increase in the yield (%) of quinoxaline (2,3-diphenylquinoxaline) was observed over HC coated catalysts. This difference in the activity of HC coated catalyst and the powder form of the same catalyst can be explained as follows: In the case of solid acids coated on HC monolith, the number of channels, their diameter and wall thickness determines the wall density, expressed as cells per square inch (cpsi). This in turn allows the calculation of the geometric surface area; the sum of the areas of all the channel walls upon which the solid acid catalyst is deposited. This leads to one of the most important advantages of the HC in that it has a large open frontal area. The lower catalyst loading in case of HC catalyst is compensated by the higher efficiency due to the good mass-transfer characterization. This may also be attributed to the availability of more active sites of the solid acid catalyst on the surface of HC due to homogenous dispersion of the catalyst, which is not possible when the catalyst is used in its powder form.

**Synthesis of quinoxaline derivatives over CZ catalyst coated on HC under optimized conditions**

After obtaining the optimized reaction conditions for the synthesis of 2,3-diphenylquinoxaline (Entry 1), the reactions were extended towards the synthesis of different quinoxaline derivatives (Table 3). The reactions were carried out over 0.05 g CZ coated on HC as a catalyst at a reaction temperature of 40 °C and in presence of EtOH: water = 3:2 as solvent. The data related to the melting point and NMR of the quinoxaline derivatives synthesized for the present work are given as Supplementary Data.
Reactivation and reusability of catalyst materials

An ideal catalytic material not only displays high catalytic activity but also offers inherent advantages, such as high stability, low deactivation rate, long life and easy regeneration. The reusability of solid acids was investigated.

The used solid acid catalyst (HC coated with CZ) recovered from the reaction mixture was washed with acetone, dried at 120 °C for 2 h and reused for the second reaction cycle in the synthesis of quinoxaline (2,3-diphenylquinoxaline) under optimized reaction conditions. Such reactivation and reusability cycles were repeated for 4 times. The reusability of the catalyst in its powder form was also reactivated and reused in the similar manner and the comparative results are shown in Fig. 3. As can be seen from the figure that the yield (%) of quinoxaline (6-phenyl-2,3-diphenylquinoxaline) over HC catalyst decreased very slightly when reused for 4 reaction cycles.

After the 4th reaction cycle, the HC catalyst coated with CZ was washed with acetone, dried at 120 °C in an oven and calcined at 550 °C for 1 h in a muffle furnace. The thermally reactivated HC catalyst was used for the next 5th and 6th reaction cycles which interestingly showed similar yield (%) of quinoxaline derivative as that of the fresh catalyst.

Further, when reusability of CZ in its HC coated form was compared with that of its powder form, the rate of decrease in the activity of CZ catalyst was more in case of its powder form of the catalyst when reused for six reaction cycle. This decrease in the activity of powder form of the catalyst can be attributed to the loss of the powder catalyst during separation or washing or filtration process. Loss of active catalyst from the surface of a honeycomb is not possible because of strong adherence of the active catalyst on the surface of the wash coated honeycomb.

This study reveals that the catalyst coated on HCs are more stable and more reusable than the solid acid catalyst in their powder forms.

Mechanism of acid catalyzed condensation of a diketone and diamine

The mechanism involves a solid acid acting as an acid catalyst in the protonation of a diketone, and also playing a role in promoting the dehydration to give a carbocationic intermediate (Scheme 2). The

![Scheme 2](image-url)

Fig. 3—Reusability of CZ in HC coated and powder forms on the yield (%) of 6-phenyl-2,3-diphenylquinoxaline. [React. cond.: React. temp. = 40 °C; wt. of the catalyst = 0.05 g of CZ coated on a HC; solvent = EtOH:water (3:2); molar ratio of DPK:OPDA = 1:1. Curve 1, HC catalyst; Curve 2, powder catalyst].
following steps are involved in the mechanism: (i) Co-ordination of a 1,2- dicarbonyl onto acid site of the solid acid, followed by (ii) the nucleophillic attack on the carbonyl carbon producing an intermediate (I), (iii) which on dehydration gives a carbocation intermediate and on elimination of a proton gives the quinoxaline product.

**Conclusions**

Ceria based solid acid catalysts coated on honeycomb monoliths were found to be efficient catalytic materials in the synthesis of quinoxaline derivatives. A correlation between the total surface acidity and the catalytic activity of the catalysts was observed. The solid acid, CeO<sub>2</sub>-ZrO<sub>2</sub> consisting of ‘moderate’ acid sites was found to be highly active in quinoxaline synthesis with 100% selectivity. However, over the solid acids such as SO<sub>3</sub>· /CeO<sub>2</sub> and SO<sub>4</sub>· /CeO<sub>2</sub>-ZrO<sub>2</sub> which comprise ‘strong’ acid sites, by-products were also formed in addition to the by-products. A correlation between the total surface acidity and the catalytic activity of the catalysts was also observed. The solid acid catalysts coated on honeycomb monoliths are very efficient materials as they are easy to prepare, easy to use, easily removable, reactive, reusable as compared to their powder forms.

**Supplementary Data**

Supplementary data associated with this article are available in the electron form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(07)843-850_SupplData.pdf.

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**References**