1. Introduction

In pharmaceutical research, methods for the synthesis of medicinally important scaffolds in high yields under moderate conditions fascinate all. Multicomponent reactions (MCRs) are one-step reactions, in which three or more starting materials are integrated together to obtain the target molecule with no need for separation of intermediates. In MCRs, the product formation takes place through reaction of multiple reactive components present in the reaction media in sequence. The main characteristics are high atom economy, eco-compatibility, and efficient forming of multiple-bonds, which are the near ideal targets in the modern organic synthesis.

Heterogeneous catalysts play a key role in the development of cost-effective and eco-friendly protocols in organic synthesis. The main benefits are the recyclability and reusability of the catalytic material, which are not observed in other organic or inorganic homogenous catalysts. The principal assets of heterogeneous catalysts are their high surface area, simple handling, low toxicity, short reaction times, easy separation, and thermal and mechanical stability, relative to many homogenous catalysts.

To vary the surface characteristics of heterogeneous catalysts, the use of mixed oxides is an attractive option. The recent literature reveals that zirconium oxide has been used either as an active material or a support in catalysts in the design of various organic transformations, with good product selectivity. ZrO$_2$ even shows potential catalyst activity in water. Its redox properties, high surface area, and acidic and basic sites make it superior to other catalytic ESI. Furthermore, ZrO$_2$ is less-expensive, stable, non-hazardous, reusable and viable available. Bismuth is a green grade element and its related compounds play a prominent role in many organic transformations, such as oxidation, reduction, and C–C bond formation reactions, owing to the presence of Lewis acidic character. Moreover, it is non-toxic and highly stable. Hence, the use of bismuth oxide-loaded zirconia catalysts is an elective choice for the present synthetic scheme.

Heterocyclic molecules have become important in the fields of pharmaceutical, agro, industrial and combinatorial chemistry. Accomplishing facile and easy methods for the design of new composite heterocyclic moieties is a key aspect and ongoing challenge in the field of heterocyclic chemistry. Pyrano[2,3-c]pyrazoles and their derivatives are significant nitrogen-containing heterocyclic molecules with interesting biological and pharmaceutical properties, such as anti-inflammatory, anticancer, antioxidant, anti-bacterial and anti-tubercular agents. Subsequently, the preparation of several substituted pyrano[2,3-c]pyrazole derivatives has been explored by different methods, using silica-supported tetramethylguanidine, BS-2G-Ti, Ba(OH)$_2$, γ-alumina, Amberlyst A21, acetic acid, visible light-assisted synthesis etc. as catalysts. All these reactions reported have low yields, with many demanding expensive chemicals, harsh reaction conditions and long reaction times. Therefore, an improvement over existing procedures with a greener approach with enhanced yields under milder conditions is necessary and vital.
With consistent interest in development of improved methods for the synthesis of different biologically active scaffolds, we have previously reported varied enriched protocols for the synthesis of novel heterocycles.29–32 In this communication, we report a new catalyst material Bi₂O₃/ZrO₂ for MCRs for the synthesis of new functionalized pyran[2,3-c]pyrazole derivatives by using a one-pot four-component reaction.

2. Experimental section

2.1 Catalyst preparation

A series of bismuth oxide-loaded zirconia (Bi₂O₃/ZrO₂) catalyst materials with different weight percentages were prepared (1, 2.5, & 5 wt%) by employing wet impregnation method.31–35 A mixture of zirconium oxide (ZrO₂, 2 g, Alfa Aesar) and an appropriate amount (wt%) of bismuth chloride (BiCl₃, Alfa Aesar) in deionised water (60 mL) was agitated with vigorous stirring at room temperature (RT) for 7 h. The resultant slurry was heated to and preserved at 75 °C for 1.5 h and then allowed to cool to RT. Then, the slurry was filtered under vacuum and dried in an oven at 120–140 °C for 8 h, and further calcined at 450 °C for 6 h in the presence of air to afford different wt% of Bi₂O₃/ZrO₂. Instrumentation details are included in the (ESI-I†).

2.2 General procedure for the synthesis of pyranopyrazole derivatives (5a–k)

In order to examine the efficiency of the prepared Bi₂O₃/ZrO₂ catalyst, in a 25 mL reaction flask at RT, an equi-molar mixture of the chosen aromatic aldehyde (1 mmol), malononitrile (1 mmol), hydrazine hydrate (1 mmol), diethyl acetylenedicarboxylate (1 mmol) and Bi₂O₃/ZrO₂ (30 mg) catalyst were added under stirring using ethanol as the solvent (5 mL) for 15 minutes (Scheme 1). The progression of the reaction was observed by TLC. After completion of the reaction, the catalyst material was recovered by simple filtration and the organic compound was separated by addition of an appropriate amount of ethanol. Then, the pure target products were obtained after evaporation of ethanol under vacuum. All the reaction products were characterised using various spectral techniques (¹H-NMR, ¹⁵N NMR, ¹³C-NMR, HRMS and FT-IR). The related details and spectra are included in the (ESI-II†).

3. Results and discussion

3.1 XRD analysis

X-ray diffraction studies were performed to analyze the phases and crystallinity size of the catalyst materials. The powdered XRD patterns of the different wt% of prepared Bi₂O₃–ZrO₂ are shown in Fig. 1 and the diffraction peaks (2 theta) were measured from 0° to 90°. The major diffraction peaks placed at 2θ of 24.5°, 27.8°, 31.3°, 35.4° and 50.3° are indexed to the (110), (−111), (111), (200) and (022) diffraction planes of ZrO₂ and the peaks were also correlated with international standard file (JCPDS 37-1484). The Bi₂O₃ peaks were displayed in the XRD diffractogram at 2θ = 27.16°, 30.3°, 35.4°, 40.3°, 46.9°, 53.4°, 56.1°, 59.4°, 62.9°, 64.5° and 65.9° and furthermore these were matched with (120), (012), (013), (302), (124), (222), (134), (052), (412) and (251) diffraction planes corresponding to the standard file (JCPDS 41-1449). The diffraction pattern reveals the polycrystalline nature of the prepared catalytic material.

3.2 TEM analysis

The TEM image of 2.5 wt% bismuth loaded on zirconia is shown in Fig. 2a. It shows that bismuth particles settled as irregular black particles on the spherical shaped zirconia particles. The highly dispersed bismuth particles occur due to fine interaction...
between bismuth and the zirconia oxides. In order to analyse the particle size distribution (Fig. 2b) quantitatively, the histogram was fitted with the Gaussian function and the mean particle size was calculated to be 8.54 nm.

### 3.3 SEM analysis

Fig. 3a displays a scanning electron microscopy (SEM) image of the Bi$_2$O$_3$/ZrO$_2$ combined, which demonstrates the catalyst surface morphology. The units are huge with oval-like irregular shapes. This microgram displays that the Bi$_2$O$_3$ particles are aggregated and accumulated on the zirconia. A homogeneous distribution of Bi$_2$O$_3$ on the surface of the ZrO$_2$ catalyst was calculated by EDS analysis (Fig. 3b), with minor but prominent quantities of surface improvement of bismuth.

### 3.4 BET surface area analysis

Fig. 4 illustrates the nitrogen adsorption–desorption isotherm of the Bi$_2$O$_3$/ZrO$_2$ catalyst material. The N$_2$ isotherm was associated to type IV, a typical H2-hysteresis loop, which describes characteristic mesoporous material lying within the $p/p_0$ range of 0.59–0.97. The BET surface area of the 2.5% Bi$_2$O$_3$/ZrO$_2$ catalyst material was shown to be 80.40 m$^2$ g$^{-1}$, pore volume 0.320 cm$^3$ g$^{-1}$ and pore size 106.4 Å. For the 1% Bi$_2$O$_3$/ZrO$_2$ catalyst loading, the particles are small and have a high surface area, but had less active sites relative to the 2.5% Bi$_2$O$_3$/ZrO$_2$. With the 5% Bi$_2$O$_3$/ZrO$_2$ loading, the bismuth particles are...
visibly larger, and hence have a smaller surface area, when compared to the 2.5% loading and thus slightly lower yield. Hence, Bi$_2$O$_3$ on ZrO$_2$ acts as a good promoter for the present transformation. These results suggest that bismuth on zirconia could act as a good promoter for the growth of additional crystalline faces, which cooperate to enhance the catalytic activity.

### 3.5 Pyridine IR analysis

The ex situ pyridine$^a$ adsorbed FT-IR spectrum in the range of 1600–1400 cm$^{-1}$ for the prepared Bi$_2$O$_3$/ZrO$_2$ is displayed in Fig. 5. The bands at 1449 cm$^{-1}$, 1487 cm$^{-1}$ and 1530 cm$^{-1}$ were attributed to Lewis, Bronsted, and Lewis and Bronsted acidic sites respectively. Upon careful examination, the prepared catalyst material reveals strong Lewis acidic and weak Bronsted acidic sites.

### 3.6 Reaction optimization

The four-component reaction protocol of substituted aromatic aldehydes, malononitrile, hydrazine hydrate and diethyl acetylenedicarboxylate using a Bi$_2$O$_3$/ZrO$_2$ catalyst is shown in Scheme 1. To optimise the reaction, decrease the reaction time and increase the product yield, the effects of variation of catalysts, solvents etc., were examined on this model reaction. Initially, the reaction of 2-methoxy benzaldehyde, malononitrile, hydrazine hydrate and diethyl acetylenedicarboxylate was conducted by using several pure metal oxide catalysts, such as SiO$_2$, ZrO$_2$ and Al$_2$O$_3$. Moderate yields were achieved (Table 1, entries 8–12). The reaction was carried out with various basic organic and inorganic catalysts, such as TEA, pyridine, DABCO, NaOH and K$_2$CO$_3$ at RT, very low yields were observed (Table 1, entries 8–12). The reaction was conducted by using several pure metal oxide catalysts, such as SiO$_2$, ZrO$_2$ and Al$_2$O$_3$. Moderate yields were afforded at RT after 2.0–3.0 h reaction time (Table 1, entries 13–15). Among the selected heterogeneous catalysts, ZrO$_2$ exhibited promising results with the highest yield (Table 1, entry 14). It is well known that mixed oxides are better catalysts compared to single oxides. Based on the results with ZrO$_2$, to improve the yield and reaction times the reaction was attempted with various mixed metal oxides (2.5% CuO/ZrO$_2$, MnO$_2$/ZrO$_2$ and Bi$_2$O$_3$/ZrO$_2$), which all gave good to excellent yields (81–98%) at RT with EtOH as the solvent (Table 1, entries 16–18), and Bi proved to be superior. Hence, the effect of varied loading of Bi$_2$O$_3$ on ZrO$_2$ was examined by using different wt% (1%, 2.5% and 5%) of Bi$_2$O$_3$ on ZrO$_2$ supports; the results were impressive with excellent yields within short times (Table 1, entries 18–20). Using 1% Bi$_2$O$_3$ loaded on ZrO$_2$ (Table 1, entry 19), the product yield was 90% in 45 min of stirring under the optimized conditions. A further increase of Bi loading (5%) led to a slightly decreased yield (96%) without any improvement in reaction time. While with 1% loading there were less active sites, the good activity with 2.5% loading may be because the dispersion of Bi$_2$O$_3$ on the surface of ZrO$_2$ is uniform; with 5% loading, oligomerisation of Bi$_2$O$_3$ on the surface of ZrO$_2$ may have happened, which decreases the activity of the sites. Thus, the catalytic activity was lower when compared with 2.5% loading. Based on this evaluation of the results, it is noticeable that 2.5% Bi$_2$O$_3$ loaded on zirconia catalyst has a higher surface area and subsequently the

### Table 1 Optimal condition for the synthesis of 5a by 2.5% Bi$_2$O$_3$/ZrO$_2$ catalyst$^a$

| Entry | Catalyst | Conditions | Time (h) | Yield$^b$ (%) |
|-------|----------|------------|---------|---------------|
| 1     | —$^c$    | RT         | 10      | 11            |
| 2     | —$^c$    | Re flux    | 10      | 12            |
| 3     | AcOH     | RT         | 9.5     | 36            |
| 4     | FeCl$_3$ | RT         | 9.5     | 41            |
| 5     | PTSA     | RT         | 9.5     | 30            |
| 6     | (Bmim)BF$_4$ | RT | 8.0 | 6            |
| 7     | $\tau$-Proline | RT | 7.0 | 8            |
| 8     | TEA       | RT         | 6.0     | 17            |
| 9     | Pyridine  | RT         | 4.5     | 21            |
| 10    | DABCO    | RT         | 5.0     | 23            |
| 11    | NaOH      | RT         | 4.5     | 20            |
| 12    | K$_2$CO$_3$ | RT     | 4.0     | 25            |
| 13    | SiO$_2$  | RT         | 3.0     | 49            |
| 14    | ZrO$_2$  | RT         | 2.0     | 76            |
| 15    | Al$_2$O$_3$ | RT | 2.5  | 58            |
| 16    | 2.5% CuO/ZrO$_2$ | RT | 1.0  | 81            |
| 17    | 2.5% MnO$_2$/ZrO$_2$ | RT | 0.90 | 88            |
| 18    | 2.5% Bi$_2$O$_3$/ZrO$_2$ | RT | 0.25 | 98            |
| 19    | 1% Bi$_2$O$_3$/ZrO$_2$ | RT | 0.75 | 90            |
| 20    | 5% Bi$_2$O$_3$/ZrO$_2$ | RT | 0.25 | 96            |

$^a$ All products were characterised by $^1$H-NMR, $^{15}$N NMR, $^{13}$C-NMR, HRMS and FT-IR spectral analyses. $^b$ Isolated yields. $^c$ — No catalyst used.
most reactive acidic sites owing to its nature and exhibited better catalytic activity compared to the other mixed catalysts. Furthermore, these catalysts have higher surface area, smaller particle sizes and more catalytic active sites than the related oxide homologues. Therefore, 2.5% Bi₂O₃/ZrO₂ catalyst was preferred for all further reactions to attain excellent product yields.

The model reaction with 2.5% Bi₂O₃/ZrO₂ was conducted using varied non-polar and polar (protic and aprotic) solvents, such as n-hexane, toluene, THF, DMF, H₂O, MeOH and EtOH, at RT (Table 2). No reaction was observed with non-polar solvents (n-hexane and toluene; Table 2, entries 1 and 2). However, polar aprotic solvents (THF and DMF) revealed a very low yield (Table 2, entries 3 and 4). Further, the reaction occurred efficiently with polar solvents (H₂O, MeOH and EtOH) and with excellent yields in short reaction times except with H₂O (Table 2, entries 5–7). When using H₂O, as a polar green solvent, the reaction time increased and the yield was decreased. Based on these results, ethanol was chosen as the ideal solvent, which is also environmentally friendly and cost-effective.

Next, the model reaction was evaluated by employing different amounts of 2.5% Bi₂O₃/ZrO₂ catalyst. The summarized outcomes (Table 3, entries 1–3) show that the increase in amount of catalyst from 10 mg to 30 mg leads to an increase in the product yield from 58% to 98% plus decreased reaction time. No significant change was observed in the yield of product with further increase in the amount of catalyst from 30 mg to 60 mg. Therefore, 30 mg of Bi₂O₃/ZrO₂ catalyst was used for the further reactions.

For the optimised reaction conditions, to establish the wider scope of the protocol, the method was applied for the synthesis of different pyranopyrazoles using various substituted aromatic aldehydes (Table S4†) and the results are summarized in Table 4. The 2.5% Bi₂O₃/ZrO₂ catalyst material catalysed the facile one-pot synthesis of pyranopyrazole derivatives with excellent yields in short reaction times (<20 min). Remarkably, the aldehydes with both electron donating and electron withdrawing (ortho, meta and para) substituents worked efficiently under the reaction conditions, producing the corresponding target products (5a–k).

4. Reusability of catalyst

The reusability and recyclability of a solid catalyst material is an important parameter as per green chemistry principles. Several recycling experiments were conducted to examine the stability and sustainability of the catalyst material. After completion of every run, filtration was employed to separate the catalyst from the crude product.

Then the catalyst was washed with ethanol and dried at 120 °C for 3 h for up to seven runs. Marginal loss of less than 5% of the catalyst was observed in the recovery procedure. Then it was washed with ethanol and dried at 120 °C for 3 h. The loss was supplemented to 30 mg by adding the minute amount required. Activity was retained with no loss in the first six runs, then the material's catalytic activity weakened by 4% in the 7th cycle. No loss of catalytic activity could be observed up to the 6th run owing to the minor losses in the recovery process and non-leaching of the active material.

5. Mechanism

In agreement with experimental results, a plausible mechanism is suggested in Scheme 2. The presence of Lewis acidity on the catalyst surface would facilitate the reaction. It may be assumed that in the first step Knoevenagel condensation is achieved by the coordination of Lewis acidic sites with the oxygen of the carbonyl group, forming a carbocation intermediate (a). In the
Scheme 2 Plausible reaction mechanism for the formation of 2,4-dihydropyrano[2,3-c] pyrazole-3-carboxylate derivatives.

Table 5 Comparison of various catalysts for the synthesis of pyrano[2,3-c]pyrazole derivatives

| Catalyst                     | Solvent | Reaction condition | Time   | Yield (%) [ref.] |
|------------------------------|---------|--------------------|--------|------------------|
| Silica-supported tetramethylguanidine | Neat    | RT                 | 15-60 min | 79-98 (ref. 22)  |
| BS-2G-Ti                     | H2O     | Heating            | 60-100 min | 45-96 (ref. 23)  |
| Ba(OH)2                      | H2O     | Reflux             | 60-120 min | 81-93 (ref. 24)  |
| γ-Alumina                    | H2O     | Reflux             | 35-90 min  | 61-90 (ref. 25)  |
| Amberlyst A21                | EtOH    | RT                 | 10-65 min  | 73-98 (ref. 26)  |
| AcOH                         | AcOH    | Reflux             | 72-90 min  | 71-92 (ref. 27)  |
| Visible light assisted       | Neat    | RT                 | 15-25 min  | 56-90 (ref. 28)  |
| 2.5% Bi2O3-ZrO2              | EtOH    | RT                 | ≈ 20 min   | 91-98 [this work]|

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next step, the active methylene group reacts with the carbocation
intermediate giving (b); next it will dissociate from the
surface taking a proton from the protic solvent (EtOH)
and giving (c). It will further undergo dehydra-
tion giving (3). In the next step, ethyl 5-oxo-2,5-dihydro-1H-pyrazole-3-carboxylate
(6) is possibly formed by the reaction between hydrazine
hydrate (5) with diethyl acetylenedicarboxylate (4). Finally,
a Michael addition between (3) and (6) occurs, yielding
the desired product selectively through 6-exo-dig cyclization.
The catalytic efficiency of the Bi2O3/ZrO2 on the title reaction in
comparison with other reported catalysts is summarized in the
Table 5.

6. Conclusion

In summary, we designed a highly efficient and cost-effective
method for the synthesis of pyranopyrazole derivatives via
a one-pot, four-component reaction in ethanol as a green
solvent, using environmentally benign Bi2O3/ZrO2 as a selective
catalyst. Of the 11 derivatives synthesised, eight are new mole-
ecules. The operational simplicity, short reaction times, high
yields, eco-friendly solvent, and mild reaction conditions make
this method attractive. Additionally, the catalyst can be easily
recovered and recycled for at least six runs without loss of e-

ciency. Moreover, expansion of the reaction scope and synthetic
and medicinal applications of this methodology are in progress
in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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