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ORIGINAL PAPER

Preparation of a superior liquid catalyst by hybridization of three solids of nanoZnO, urea, and choline chloride for Knoevenagel-based reactions

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Abstract The complex catalyst of $[ZnClO.urea]^{-}[Ch.urea]^{+}$ has been prepared by dissolving of nanoZnO in choline chloride:2urea at 50 °C. The concentration of $[ZnClO.urea]^{-}$ in the given liquid is 19,987 ppm and 10.5 times higher than similar solution made from bulk ZnO. This organic/inorganic hybrid catalyst represents a high catalytic performance in Knoevenagel-based synthesis of pyrans, chromenes, and electron-deficient alkenes. Due to the high diffusion of ZnO nanoparticles in DESs, synergy of nanoZnO with DESs, and much contact of this fluid catalyst with starting materials, all Knoevenagel-based reactions occur with higher yields at lower catalyst loading and shorter times than individual ChCl:2urea, nanoZnO, or even previously catalysts used for this purpose. High polarity and reusability are other advantages of anionic complex $[ZnClO.urea]^{-}$ and homogenized shape of nanoZnO.

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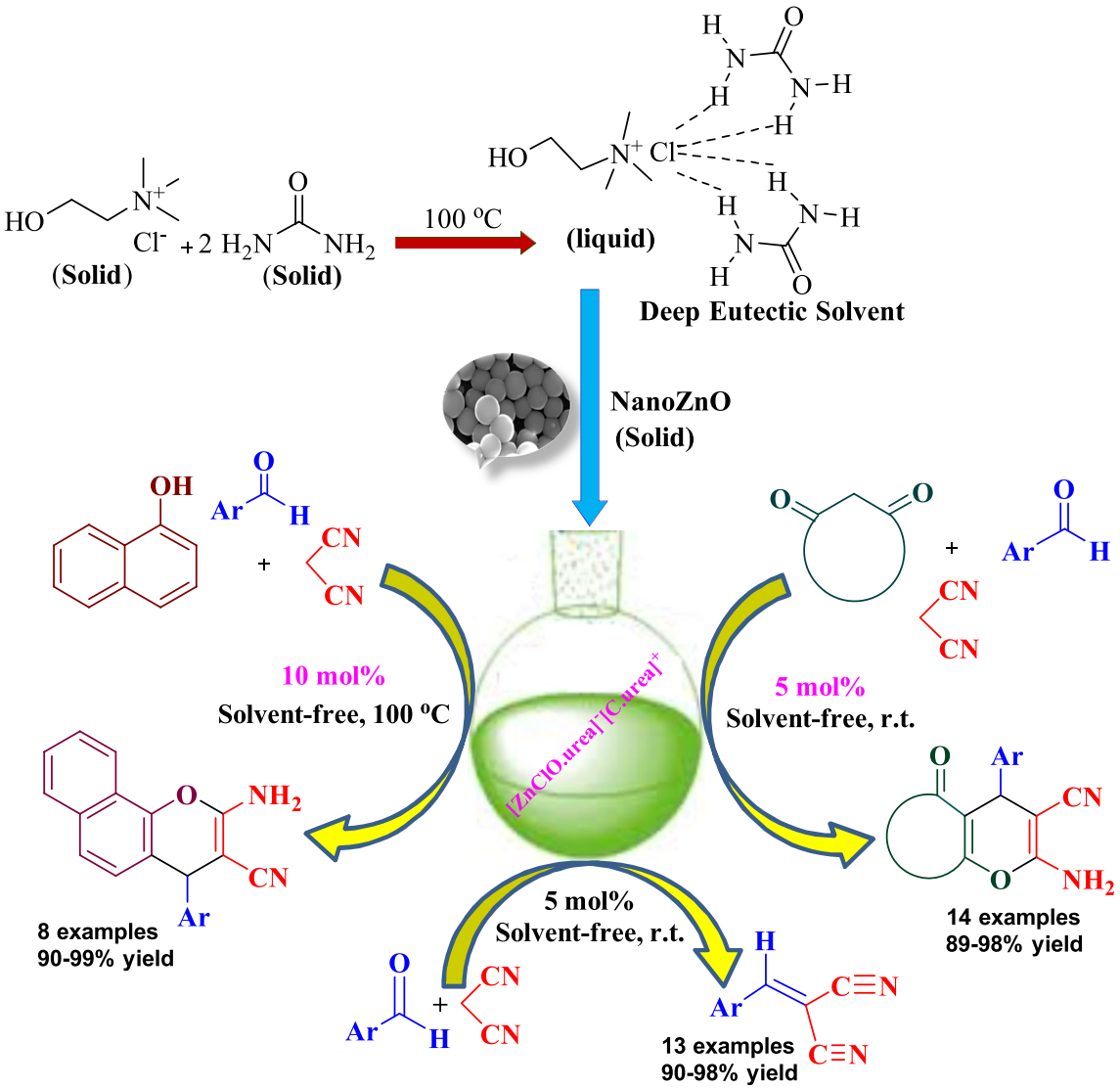
Graphical Abstract



Keywords Deep eutectics · NanoZnO · [ZnClO.urea]$^{-}$[Ch.urea]$^{+}$ · Chromenes · Pyrans · Knoevenagel

Introduction

In the past decade, design of hybrid catalysts with profits of homogeneous and heterogeneous materials has been the core of chemical researches [1–4]. Nanometal oxides (NMO) are of these bridge catalysts that have been extensively settled to promote organic transformations [5]. The available catalytic sites of NMOs depend on their particle size, morphology, and aggregation type [6]. NanoZnO is an amphoteric NMO catalyst that has been used for acceleration of organic reactions [7–14]. Due to the maximum active sites of nanoZnO in fluid shape and closest structure of fluids to homogeneous catalysts, design and use of these dual incentive NMO-fluids is highly desirable.

Deep eutectic solvents (DESs) are more advantageous alternatives for high cost and toxic ionic liquids (ILs) that originally designed to reply to environmental challenges [15–17]. DESs are very polar liquids made from two or more low-priced solids that interact with each other by >200 °C depression of melting points [18–22]. Owing to cheapness, biodegradability, and non-toxicity of choline chloride (ChCl) and urea, ChCl:2urea is among the most favorite DESs that their ability to dissolving of zinc oxide as anionic complexes of [ZnClO.urea]$^{-}$ and $ZnCl_3^{-}$ confirmed by Abbott et al. [18–22]. These anionic complexes have been specified in solubilized ZnO in ChCl:2urea and ChCl:malonic acid by mass spectroscopy, while concentration of [ZnClO.urea]$^{-}$ and

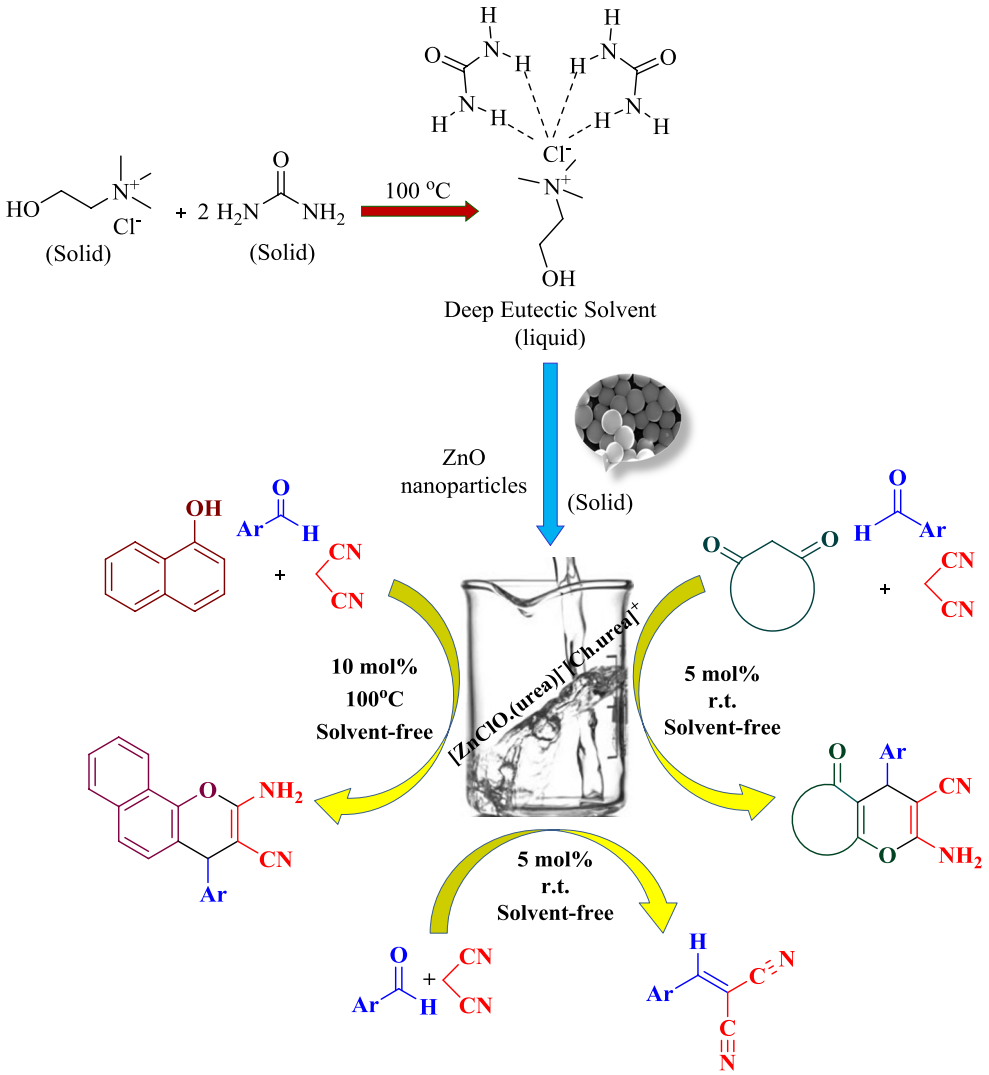
$ZnCl_3^-$ has been determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [21, 22].

Pyrans [26–29] and chromenes are biologically active multifunctional molecules that have been prepared by Knoevenagel-based multi-component reactions (MCRs) which pass through electron-deficient Michael-acceptor intermediates [35–40]. Due to the importance of pyrans and chromenes, their synthesis has been developed using various acid/base catalysts and conditions, though development of new hybrid organic/inorganic catalysts for more efficient synthesis of these compounds is desirable. Herein, for the first time, we hybridized nanoZnO and eutectics to give nanofluid catalysts containing high concentration of $[ZnClO.urea]^-$ and $ZnCl_3$ complexes and used very low loading of the new hybrid catalyst of nanoZnO/ChCl:2urea in advanced synthesis of electron-deficient alkenes [23–25], pyrans [26–29] and chromenes [30–34] (Scheme 1).

Results and discussion

Initially, for a more efficient preparation of anionic complexes $[ZnClO.urea]^-$ and $ZnCl_3^-$, nanoZnO was prepared by following a previous method [11], while the surface area of the given nanoZnO was 33.6 m^2/g and higher than 5 m^2/g for ZnO in commercial grade. The characteristic narrow peaks of the (100), (002), (101), (102), (110), (103), (112), (201), and (004) at various 2θs from 30° to 80° in the XRD pattern of the given nanoZnO are compatible with standard JCPDS 36-1451 indexed for hexagonal wurtzite ZnO [41]. The strong intensities of these peaks show high crystallinity of the prepared nanoZnO (Fig. 1).

The FESEM image of nanoZnO also displays a mixture of flake, disk, and rod surface morphologies with some hexagonal wurtzite cross sections in nano-dimensions (Fig. 2).



Scheme 1 Catalytic usage of nanoZnO/ChCl:2urea in Knoevenagel-based reactions

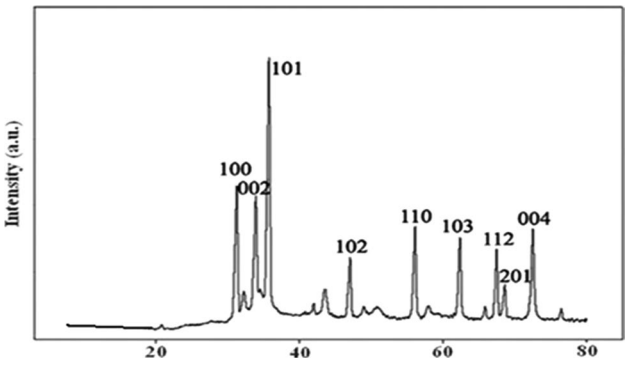


Fig. 1 XRD pattern of the prepared nanoZnO

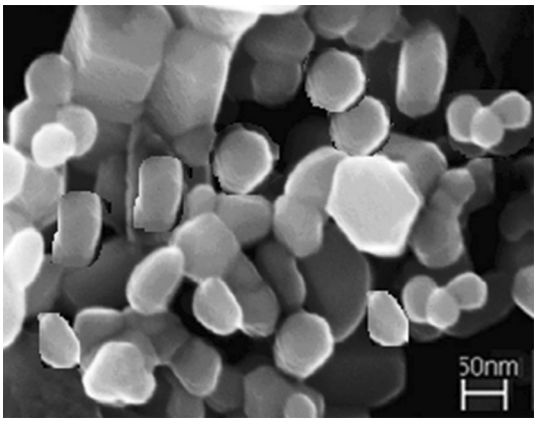


Fig. 2 The FESEM of the prepared nanoZnO

Then 0.08–1.44 g of nanoZnO was dissolved in 5 mL of freshly made ChCl:2urea or ChCl:malonic acid DESs at 50 °C to give one-phase clear viscose solutions of [ZnClO.urea]$^-$ or chlorometalate of $ZnCl_3^-$ [20–22]. These solutions were stable and did not change by even high-speed centrifugation. To assign the above anionic complexes, which have been documented earlier by Abbot et al. [21, 22] in the given fluid, various spectroscopic techniques were employed. For example, characterized peaks at various m/z = 174 (base peak), 176, and 178 in mass spectrum of a sample prepared from nanoZnO (1.44 g) and ChCl:2urea (5 mL) and typical peaks at m/z = 1176, 174, 172, and 170 (base peak) in mass spectrum of the given nanofluid from nanoZnO (1.44 g) and ChCl:malonic acid (5 mL) were compatible with previous reports on anionic complexes of [ZnClO.urea]$^-$ and $ZnCl_3$ [21, 22]. Typically, the FT-IR spectrum of the fluid given from 1.44 g nanoZnO and uDES (5 mL) shows all vibrational modes of functional groups of nanoZnO, urea, and choline chloride-based materials in Fig. 3. Thus, adsorption band at ~500 cm^{-1} is respected to Zn–O stretching, the well-defined bands at 3342– 3408 and 3205 cm^{-1} are due to overlapped stretchings NH_2/OH in uDES, and the strong bands at 1670 and 1620 cm^{-1} are assigned to C=O stretching and N–H bending, respectively (Fig. 3d).

Similarly, elemental analysis of this hybrid catalyst showed 30.01% C, 7.80%H, and 19.05%N, which are very close to calculated percent of elements for this fluid as 29.12%C, 7.60% H, 9.55% Cl, 18.87% N, 17.24% O, and 17.6% Zn. According to these results, the following structure is proposed for nanoZnO/ChCl:2urea as complex of [ZnClO.(urea)]$^-$[Ch.urea]$^+$ (Scheme 2).

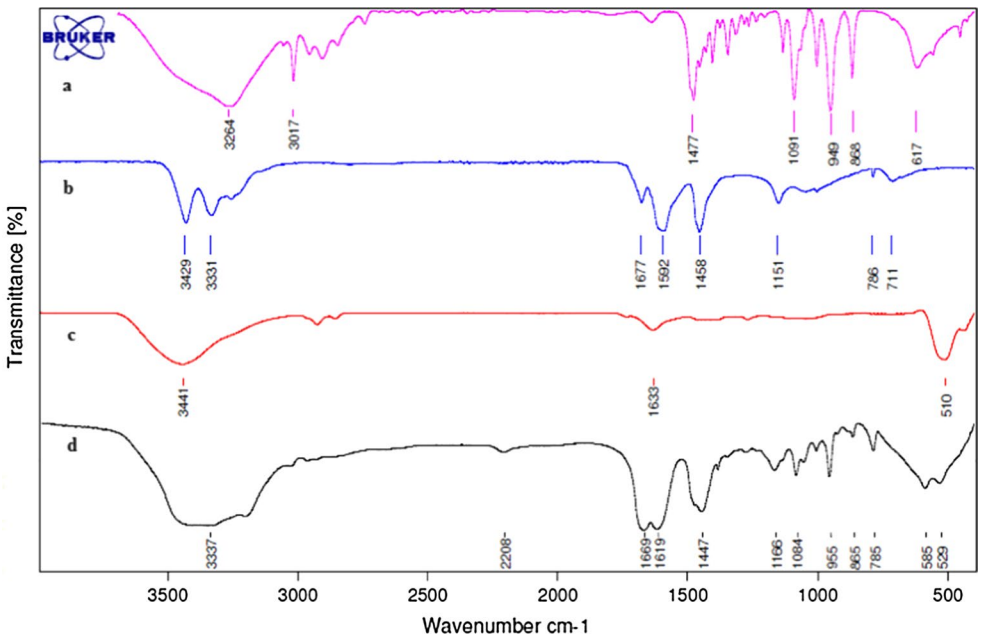
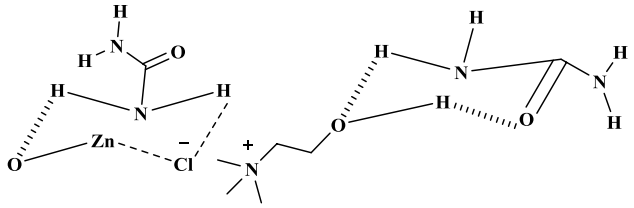
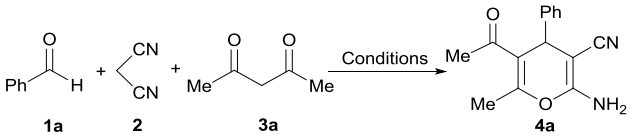


Fig. 3 FT-IR spectra of **a** ChCl **b** urea **c** nanoZnO **d** nanoZnO/uDES



Scheme 2 Proposed structure for anionic complex $[ZnClO.urea]^-$ formed in nanoZnO/ChCl:2urea

Table 1 Optimization of Reaction Conditions



Entry	Conditions Catalyst (mol%)/Solvent/Temp. (°C)	Time (h)	Yield (%)[a]
1	-/-/r.t.[b]	24	Trace
2	ZnO (10)/-/r.t.	3	63
3	ZnO/ChCl:2urea (10)/-/r.t.	3	80
4	ChCl (10)/-/r.t.	3	52
5	ChCl:2urea (10)/-/r.t.	3	65
6	ChCl:malonic acid (10)/-/r.t.	3	25
7	nanoZnO (10)/-/r.t.	3	80
8	$[ZnCl_3]^-$[Ch.malonic acid]$^+$ (10)/-/r.t.	3	30
9	$[ZnCl_3]^-$[Ch.malonic acid]$^+$ (20)/-/r.t.	3	35
10	$[ZnClO.urea]^-[Ch.urea]^+$ (2.5)/-/r.t.	1	70
11	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/-/r.t.	0.15	95
12	$[ZnClO.urea]^-[Ch.urea]^+$ (10)/-/r.t.	0.15	92
13	$[ZnClO.urea]^-[Ch.urea]^+$ (20)/-/r.t.	0.15	85
14	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/-/40	0.15	94
15	$[ZnClO.urea]^-Ch.urea]^+$ (5)/-/60	0.15	90
16	$[ZnClO.urea]^-Ch.urea]^+$ (5)/-/80	0.15	90
17	$[ZnClO.urea]^-Ch.urea]^+$ (5)/H_2O/r.t.	1	68
18	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/EtOH/r.t.	1	84
19	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/CH_3CN/r.t.	2	50
	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/$CHCl_3$/r.t.	4	42

[a] Isolated yield

[b] Room temperature

The ICP-AES experiments showed that replacing nanoZnO with ZnO leads to growth in solubility of this metal oxide in ChCl:2urea, so the concentration of $[ZnClO.urea]^-$ from 1894 ppm at 50 °C for bulk ZnO [22] reached to 19,987 ppm for nanoZnO in this work. The given clear and viscose solution was stable at room temperature and remained liquid even by high-speed centrifugation.

Table 2 Comparative Performances of $[ZnClO.urea]^-[Ch.urea]^+$ in Synthesis of **4a**

Entry	Conditions Catalyst(mol%)/Solvent/Temp (°C)	Time (h)	Yield (%)[Ref].
1	nanoZnO (10)/EtOH:H_2O/r.t.	3.5	92 [26]
2	ChCl:2urea (excess)/80	4	82 [27]
3	$[ZnClO.urea]^-[Ch.urea]^+$ (5)/-/r.t.	0.15	95 (This work)

To evaluate the catalytic activity of fluidic complexes of $[ZnClO.urea]^-$ and $ZnCl_3^-$, typical three-component reaction of benzaldehyde (**1a**), malononitrile (**2**), and acetyl acetone (**3a**) for synthesis of pyran **4a** was attempted with these catalysts under various conditions (Table 1).

The maximum catalytic activity in terms of reaction time and yield was for 5 mol% of $[ZnClO.(urea)]^-[Ch.urea]^+$ at room temperature (Table 1, entry 11). The superiority of this complex versus other catalysts is attributed to its high polarity, stability, homogeny, and its chemical structure for better diffusion to reaction mixture and activation of starting materials.

However, Table 2 shows the catalytic performance of $[ZnClO.urea]^-[ChCl.urea]^+$ versus recently reported protocols for synthesis of **4a**.

The recoverability and reusability of homogeneous catalysts is an important challenge in catalysis issues and industrial usage of catalyst. Due to the insolubility of DESs in EtOAc, for reusability test of $[ZnClO.(urea)]^-[Ch.urea]^+$, after the first run of the model reaction in 50 mmol scale, EtOAc was added, product **4a** was extracted, the remained catalyst was washed with EtOAc, dried under vacuum, and reused with a poor loss of activity after the third reaction run (Fig. 4).

The comparative FT-IR of the recycled and fresh catalysts support no significant changes in vibrational bands of recycled catalyst and confirms the preservation of the structure of catalyst after extraction of product by EtOAc (Fig. 5).

Next the prepared complex of $[ZnClO.urea]^-[Ch.urea]^+$ was tested in the efficient synthesis of pyrans (Table 3).

According to the results, aldehydes bearing electron-withdrawing groups react faster than substrates bearing electron-donating groups, due to much positivity of carbonyl group in these molecules. The order of reactivity observed for activated methylene groups was due to dimedone > acetyl acetone > and ethyl acetoacetate which is in agreement with their acidity. Mechanistically, we proposed the following roles for $[ZnClO.urea]^-[Ch.urea]^+$ in each step of the synthesis of pyrans (Scheme 3).

The versatility of this homogeny shape of nanoZnO was also demonstrated in MCR synthesis of 2-amino-4*H*-chromenes (Table 4).

The results in Table 4 show that reactions with aldehydes bearing electron-withdrawing and electron-donating groups occurred quickly to give the corresponding products.

Similarly, synthesis of *tri*-substituted alkenes was attempted by Knoevenagel condensation of aldehydes with malononitrile in the presence of this catalyst (Table 5).

As results show, Knoevenagel products were isolated in excellent yields from the reaction of various aldehydes and malononitrile using a small amount of catalyst.

To set up the mechanism for the $[ZnClO.(urea)]^-[Ch.urea]^+$-catalyzed synthesis of pyrans and chromenes, the isolated 2-benzylidenemalononitrile **7a** from the reaction of benzaldehyde and malononitrile (Table 5, entry 1) reacted with either acetylacetone or 1-naphthol under

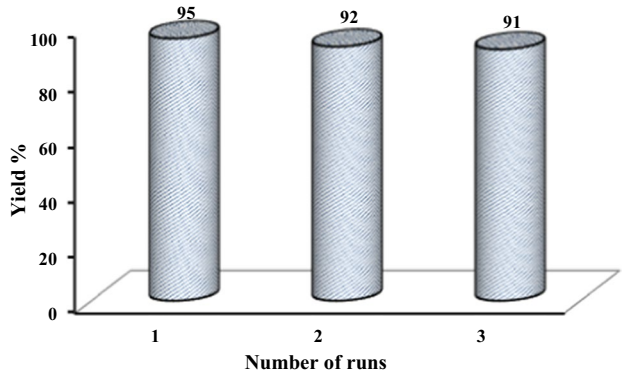


Fig. 4 Reusability of $[ZnClO.urea]^-[Ch.urea]^+$ in nanoZnO/Ch:2urea

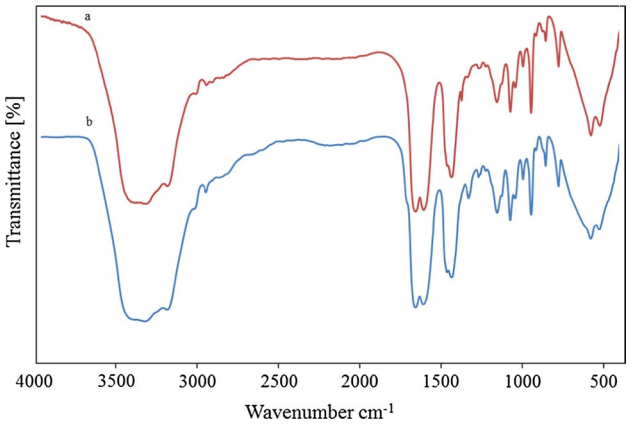
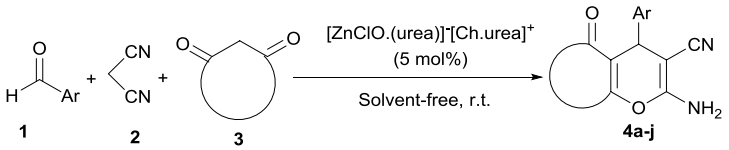


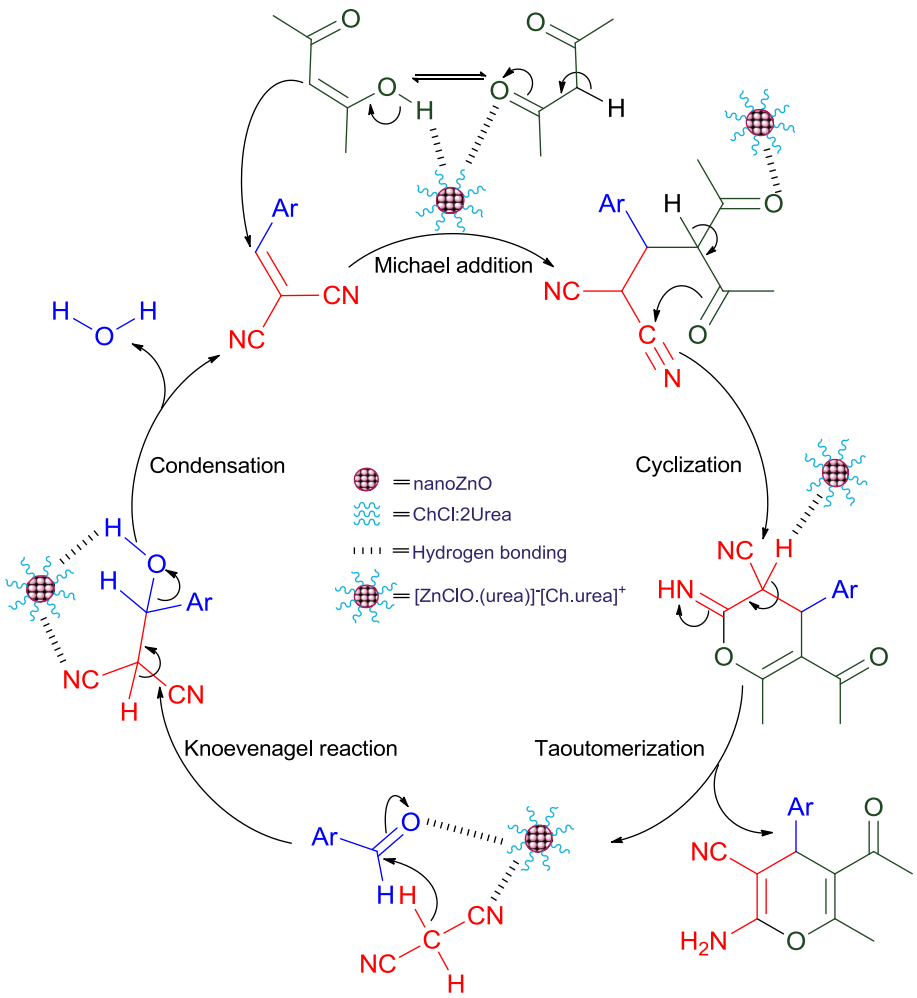
Fig. 5 Comparative FT-IR spectra of the fresh and recycled catalyst

Table 3 Synthesis of Polysubstituted 4*H*-Pyrans using $[ZnClO.urea]^-[Ch.urea]^+$



Entry	Ar	**3**	Product	Time (min)	Yield (%)[a]	m.p. (°C)/(lit.)
1	C_6H_5	Acetyl acetone	**4a**	10	95	162–163 (164) [26]
2	4-$O_2NC_6H_4$	Acetyl acetone	**4b**	30	92	169–170 (170) [26]
3	4-ClC_6H_4	Acetyl acetone	**4c**	10	98	153–155 (154) [26]
4	4-$H_3COC_6H_4$	Acetyl acetone	**4e**	100	92	156–158 (156) [26]
5	4-FC_6H_4	Acetyl acetone	**4d**	15	96	140 (140) [26]
6	4-$CH_3C_6H_4$	Acetyl acetone	**4f**	90	93	136–137 (136) [26]
7	C_6H_5	Ethyl acetoacetate	**4g**	120	95	192–194 (192) [26]
8	4-$O_2NC_6H_4$	Ethyl acetoacetate	**4h**	60	89	180–181 (182) [26]
9	4-ClC_6H_4	Ethyl acetoacetate	**4i**	90	98	170–171 (170) [26]
10	4-$H_3COC_6H_4$	Ethyl acetoacetate	**4j**	120	95	136–139 (134–136) [27]
11	C_6H_5	Dimedone	**4k**	20	96	232–234 (233) [27]
12	4-$O_2NC_6H_4$	Dimedone	**4l**	40	94	181–183 (180–182) [27]
13	4-ClC_6H_4	Dimedone	**4m**	20	97	214–216 (214–217) [27]
14	4-$H_3COC_6H_4$	Dimedone	**4n**	80	92	200–202 (195–199) [27]

[a] Isolated yield



Scheme 3 Proposed mechanism for $[ZnClO.urea]^{-}[Ch.urea]^{+}$-catalyzed synthesis of pyrans

similar conditions and the desired products **4a** and **6a** were isolated quantitatively after 15 min. This supports the presence of Michael-acceptor intermediate **7a** in these $[ZnClO.(urea)]^{-}[Ch.urea]^{+}$-catalyzed MCRs (Scheme 4).

In summary, all three types high-yielding organic reactions occurred at the shortest possible time in the presence of $[ZnClO.urea]^{-}[Ch.urea]^{+}$ to give the oxygenated heterocycles of pyrans and chromenes as well as substituted alkenes which are excellent Michael-acceptor intermediates.

Experimental

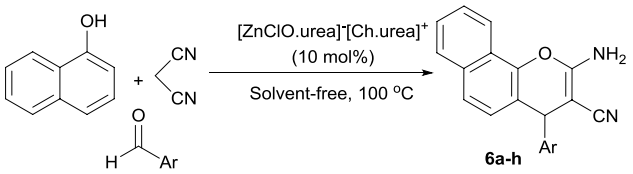
Preparation of ZnO-nanofluids

The deep eutectics were typically prepared by stirring a mixture of ChCl (10 mmol, 1.4 g) with a hydrogen bond donor like urea (20 mmol, 1.2 g) or malonic acid (10 mmol, 1.1 g) at 100 °C to give a clear liquid [22], while nanoZnO was prepared by following a previous procedure [11]. To prepare the designed nanofluids, nanoZnO (0.85 g) with mean particle size of 38–60 nm was magnetically dispersed in 10 mL of prepared DESs as fluid's base for 5 h at 50 °C. Only for ChCl:2urea a homogeny clear viscose solution was obtained and dispersion of nanoZnO in Ch:malonic acid resulted in the suspensions with no agglomeration or sedimentation of nanoparticles.

Characterization of ZnO-nanofluids

To characterize the ZnO-nanofluids, the prepared nanoZnO was firstly specified by surface area (BET), X-ray diffraction (XRD), field emission scanning electron micrograph (FESEM), and comparative FT-IR spectra of ChCl, urea, nanoZnO and $[ZnClO.(urea)]^{-}[Ch.urea]^{+}$.

Table 4 The $[ZnClO.urea]^-[Ch.urea]^+$-Catalyzed Synthesis of 4*H*-Chromenes



Entry	Ar	Product	Time (min)	Yield (%)[a]	m.p. (°C) (lit.)
1	C_6H_5	**6a**	30	91	210–211 (210–212) [30]
2	4-$O_2NC_6H_4$	**6b**	40	99	233–235 (235–236) [30]
3	4-FC_6H_4	**6c**	5	97	230–232 (229–231) [30]
4	4-ClC_6H_4	**6d**	5	98	284–285 (284–286) [30]
5	2,4-$Cl_2C_6H_3$	**6e**	30	93	222–224 (223–225) [30]
6	3-$H_3COC_6H_4$	**6f**	120	97	230–232 (232–233) [31]
7	4-$H_3COC_6H_4$	**6g**	20	97	186–188 (188–190) [30]
8	4-$H_3CC_6H_4$	**6h**	15	90	203–205 (202–204) [30]

[a] Isolated yield

General procedure for synthesis of 4H-pyrans and 2-amino-4*H*-chromenes

For synthesis of pyrans, a mixture of malononitrile (5 mmol), aldehyde (5 mmol), active methylene dicarbonyl compound (5 mmol), and ZnO-nanofluid $[ZnClO.(urea)]^-[Ch.urea]^+$ (5 mol%) was stirred at room temperature for the given times. For synthesis of 2-amino-4*H*-chromenes, a mixture of benzaldehyde (10 mmol), 1-naphthol (10 mmol), malononitrile (10 mmol), and ZnO-nanofluid (10 mol%) was stirred at 100 °C. After the completion of each reaction (TLC monitoring), EtOAc was added, the mixture was decanted, and the product was isolated by evaporation of the solvent under vacuum. The structures of the products were compatible with those reported in the literature.

General procedure for the synthesis of arylidene malononitriles

A mixture of malononitrile (5 mmol), aldehyde (5 mmol) and $[ZnClO.(urea)]^-[Ch.urea]^+$ (5 mol%) was stirred at room temperature for the given times (Table 5). After completion of the reaction, the product was isolated as above. The structures of all products were compatible with those reported in the literature.

5-Acetyl-2-amino-6-methyl-4-(4-nitrophenyl)-4H-pyran-3-carbonitrile (Table 3, entry 2)

Yellow crystal; yield 92%; m.p. 169–170 °C, IR (KBr): ν_{max} 3441, 3338, 3195, 2193, 1663, 1344, 1219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.14 (3H, s, CH_3), 2.37 (3H, s,CH_3), 4.57 (1H, s, CH), 6.13 (2H, s, NH_2), 7.38 (2H, d, J = 18.7 Hz, ArH), 8.20 (2H, d, J = 18.7 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 24.7, 29.6, 30.0, 115.2, 124.0, 124.4, 124.7, 127.2, 128.1, 129.1, 129.9, 161.5, 197.5 ppm.

5-Acetyl-2-amino-6-methyl-4-(4-fluorophenyl)-4H-pyran-3-carbonitrile (Table 3, entry 5)

Yellow crystal; yield 96%; m.p. 140 °C, IR (KBr): ν_{max} 3396, 3329, 3203, 2925, 2199, 1694, 1668, 1600, 1220 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.07 (3H, s, CH_3), 2.24 (3H, s, CH_3), 4.51 (1H, s, CH), 6.89 (2H, s, NH_2), 7.16 (2H, t, J = 110 Hz, ArH), 7.22 (2H, dd, J_1 = 110, J_2 = 16, ArH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.9, 30.3, 38.5, 58.1, 115.4, 115.9, 120.2, 129.5, 141.3, 155.3, 158.7, 161.5, 198.8 ppm.

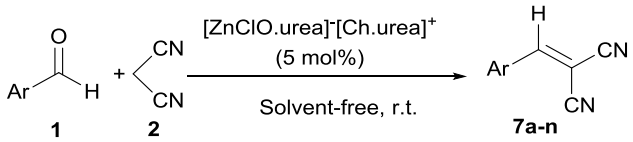
2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-4a,5,6,7,8,8a-hexahydro-4H-chromene-3-carbonitrile (Table 3, entry 12)

White solid; yield 94%; m.p. 181–183 °C, IR (KBr): ν_{max} 3397, 3322, 2191, 1683, 1654, 1522, 1347, 1215 cm^{-1};^1H NMR (400 MHz, DMSO-d_6): δ 0.96 (3H, s, CH_3) 1.04 (3H, s, CH_3),2.12 (1H, d, J = 116 Hz, CH), 2.27 (1H, d, J = 116 Hz, CH), 2.50 (2H, s, CH_2), 4.37 (1H, s, CH), 7.18 (2H, s, NH_2), 7.45 (2H, d, J = 18.3 Hz, ArH), 8.17 (2H, d, J = 18.3 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ 13.7, 20.5, 27.1, 28.4, 31.7, 35.5, 50.0, 58.3, 59.7, 112.2, 118.7, 123.2, 128.2, 146.3, 151.1, 158.3, 162.3, 195.4 ppm.

2-Amino-4-(4-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (Table 4, entry 4)

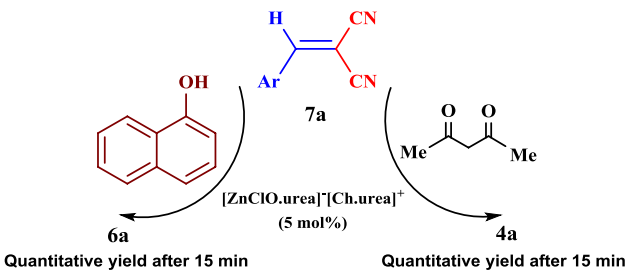
Pale yellow solid, yield 98%; m.p. 284–285 °C, IR (KBr): ν_{max} 3454, 3333, 2191, 1663, 1598, 1573, 1375, 1096, 801 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 4.95 (1H, s, CH), 7.09 (1H, d, J = 18.5 Hz, ArH), 7.21 (2H, s, NH_2), 7.28 (2H, d, J = 18 Hz, ArH), 7.38 (2H, d, J = 18 Hz, ArH), 7.62 (3H, m, ArH), 7.89 (1H, d, J = 18 Hz, ArH), 8.25 (1H, d, J = 18.3 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ 40.9, 58.9, 116.7, 120.2, 120.9,

Table 5 [ZnClO.urea]$^-$[Ch.urea]$^+$-Catalyzed Synthesis of *Tri*-Substituted Alkenes



Entry	Ar	Product	Time (min)	Yield (%)[a]	m.p. (°C)/(lit.)
1	C_6H_5	7a	5	95	82–84 (82–83) [24]
2	4-$O_2NC_6H_4$	7b	1	98	133–135 (135) [23]
3	4-FC_6H_4	7c	1	93	126–128 (125–126) [24]
4	4-ClC_6H_4	7d	2	95	162–163 (161–163) [24]
5	2,4-$Cl_2C_6H_3$	7e	3	90	148–150 (149) [23]
6	4-$CH_3C_6H_4$	7f	7	92	132–134 (134–135) [24]
7	3-$H_3COC_6H_4$	7g	3	93	106–108 (107–108) [25]
8	4-$H_3COC_6H_4$	7 h	5	90	115–116 (113–114) [24]
9	4-$(Me)_2N$ C_6H_4	7i	7	97	189–191 (190–191) [25]
10	2,4-$(MeO)_2C_6H_3$	7j	5	91	140–142 (141–142) [25]
11	4-HOC6H4	7k	5	96	188–189 (187–188) [24]
12	2-furyl	7l	5	92	72–74 (71–72) [24]
13	4-pyridyl	7n	7	94	100–102

[a] Isolated yield



Scheme 4 Confirmation of intermediate **7a** in the synthesis of pyrans and chromenes

123.2, 124.4, 125.9, 126.6, 126.8, 127.6, 128.8, 129.4, 132.8, 133.2, 143.3, 143.4, 159.7 ppm.

2-Amino-4-(4-methoxyphenyl)-4H-benzo[h] chromene-3-carbonitrile (Table 4, entry 7)

Yellow solid; yield 97%; m.p. 186–188 °C, IR (KBr): ν_{max} 3442, 3300, 3181, 2202, 1653, 1371, 1094, 805, 736, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.76 (3H, s, CH_3), 4.90 (1H, s, CH), 7.12 (1H, d, J = 18.5 Hz, ArH), 7.14 (2H, s, NH_2), 7.24 (2H, m, ArH), 7.32 (2H,

t, $J = 17.5$ Hz, ArH), 7.63 (3H, m, ArH), 7.89 (1H, d, $J = 18.1$ Hz, ArH), 8.25 (1H, d, $J = 18.3$ Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 40.7, 55.1, 59.3, 114.0, 117.5, 120.4, 120.9, 123.2, 124.1, 126.1, 126.4, 126.5, 127.5, 129.0, 133.0, 137.2, 143.1, 158.5, 159.6 ppm.

1,1-Dicyano-2-(pyridine-4-yl)ethylene (Table 5, entry 13)

White needles; yield 94%; m.p. 100–102 °C, IR (KBr): ν_{max} 3023, 2933, 2233, 1610, 1590, 1548, 1416, 1403, 1236, 1219, 1067, 933, 947, 819, 771, 621 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (2H, d, $J = 15.3$ Hz, ArH), 7.83 (1H, s, VinylH), 8.88 (2H, d, $J = 15.3$ Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.0, 111.7, 112.9, 123.0, 137.4, 151.9, 158.0 ppm.

Conclusions

In conclusion, we have developed a proficient method for preparation and application of $[ZnClO.urea]^-$ in a homogenized nanoZnO-fluid that have dual catalytic advantageous of either DESs or nanoZnO. This polar and reusable hybrid catalyst represents multiple roles in Knoevenagel-based reactions for rapid synthesis of substituted pyrans, chromenes, and electron-deficient alkenes.

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