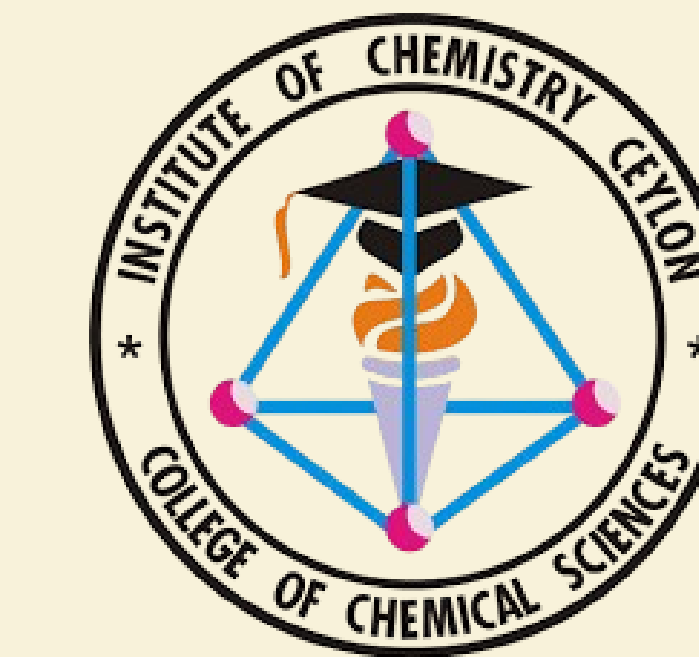
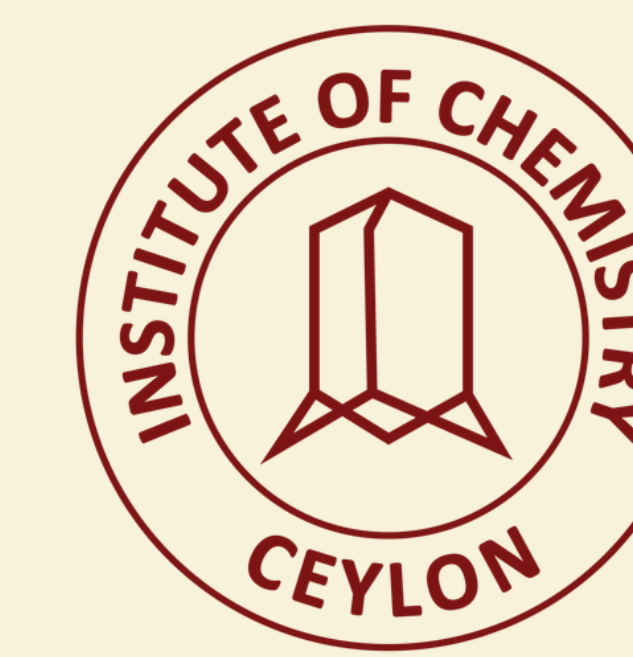


Sustainable Synthesis of Zinc Oxide Nanoparticles from Spent Coffee Grounds as a Reusable Catalyst in Biginelli Reaction

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Introduction and Aim

A multicomponent reaction (MCR) is a one-pot reaction where three or more reactants combine to form a product that incorporates most of their atoms. They are important for their atom economy, step efficiency, and reduced waste, but often require strong acid and high temperature. The Biginelli reaction is a MCR that condenses an aryl aldehyde, a β -keto ester, and urea to give dihydropyrimidinones (DHPMs). Metal nanoparticles synthesized using plant waste offer a sustainable and reusable heterogeneous catalytic alternative to conventional acids, combining low toxicity, easy separation, and alignment with circular economy principles. [2]

Biginelli Reaction

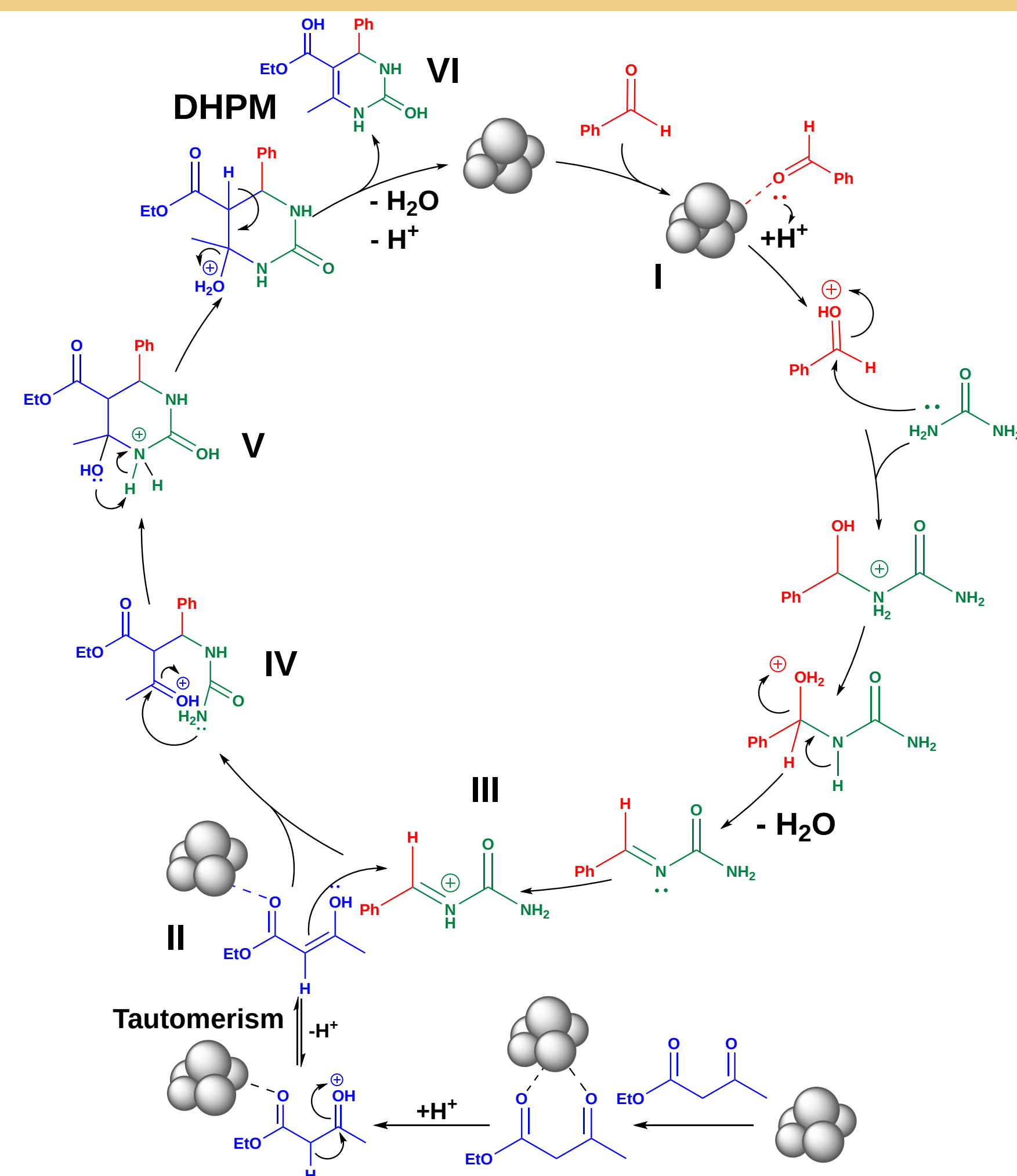


Figure 1: Mechanism of DHPM synthesis.

The presence of ZnO increases the electrophilicity of the carbonyl carbon in the aryl aldehyde (I) and ethyl acetoacetate via coordination to oxygen, making the β -keto ester's enol form (II) more available for nucleophilic attack.

In the first step, urea attacks the activated aryl aldehyde forming a N-acyliminium intermediate (III). The α -carbon of the enolate ethyl acetoacetate attacks the N-acyliminium carbon followed by another nucleophilic attack on the β -carbon by the free amidic group of urea (IV) to form a heterocyclic intermediate (V), which dehydrates a water molecule to the resultant DHPM (VI).

Materials and Methods

Spent coffee grounds were washed with deionized water, oven-dried at 80 °C overnight, and stored in an airtight container. The SCG extract was prepared by mixing SCG in deionized water at 100 °C for 10 minutes under constant stirring, followed by filtration to obtain the aqueous extract.

Following a modified procedure, SCG extract, $[\text{Zn}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ and NaOH were mixed at 1:1:2 molar ratio to synthesize ZnO NPs via the co-precipitation method at pH 9. The precipitate was isolated by centrifugation, washed with deionized water until the washings were neutral, and oven-dried at 80 °C to yield ZnO NPs.

To assess their catalytic performance in the Biginelli reaction, ZnO NPs were introduced into a mixture of aryl aldehyde, ethyl acetoacetate, and urea in a molar ratio of 1:1.1:2, respectively, in minimum ethanol and refluxed at 80 °C. The reaction progress was monitored by TLC. Upon completion, the catalyst was recovered by hot gravity filtration, while the product precipitated on cooling, was isolated by filtration, and recrystallized from ethanol.

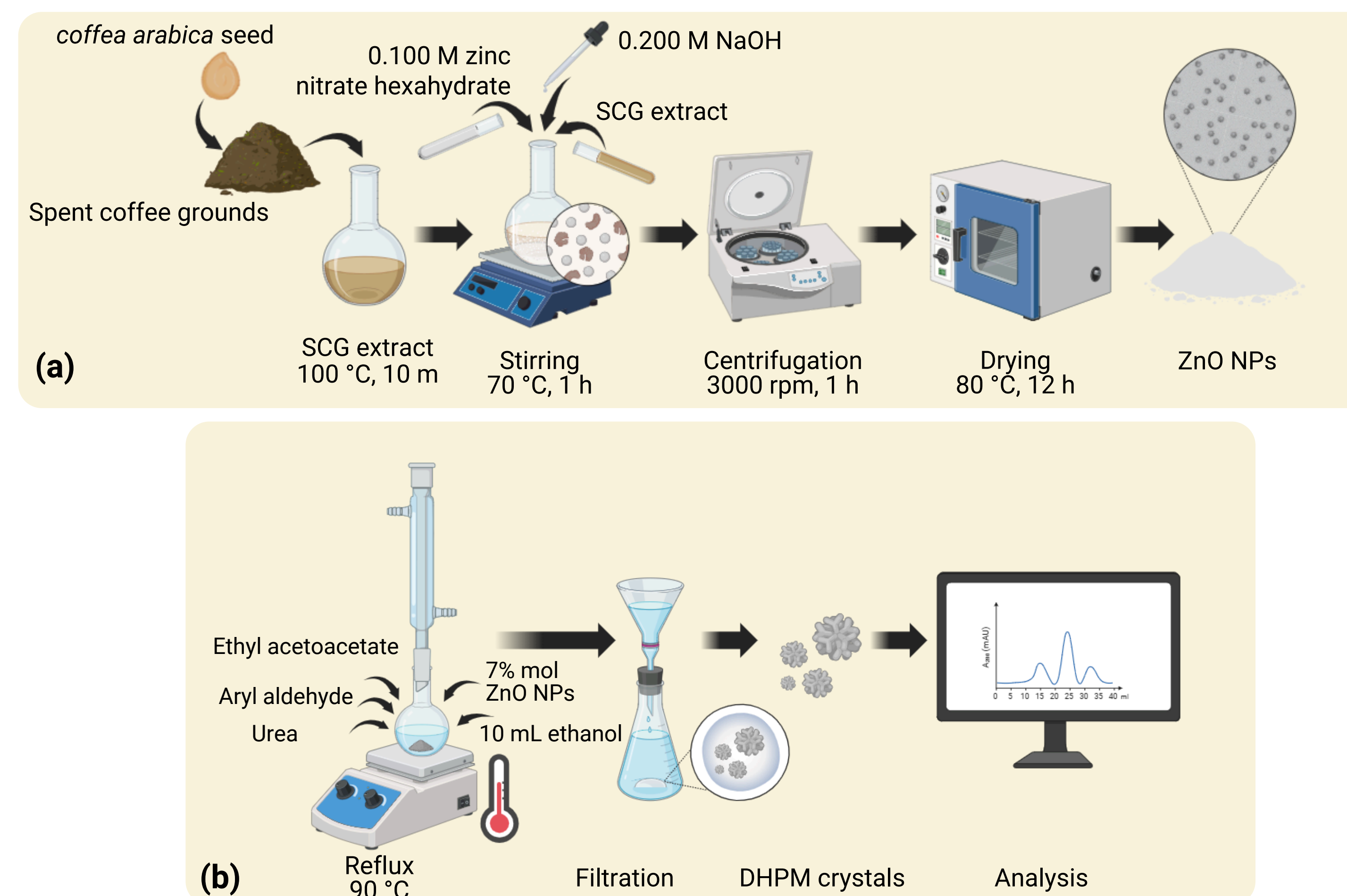


Figure 2: (a) Preparation of ZnO NPs and (b) Synthesis of DHPMs using ZnO NPs as a heterogeneous catalyst.

Results and Discussion

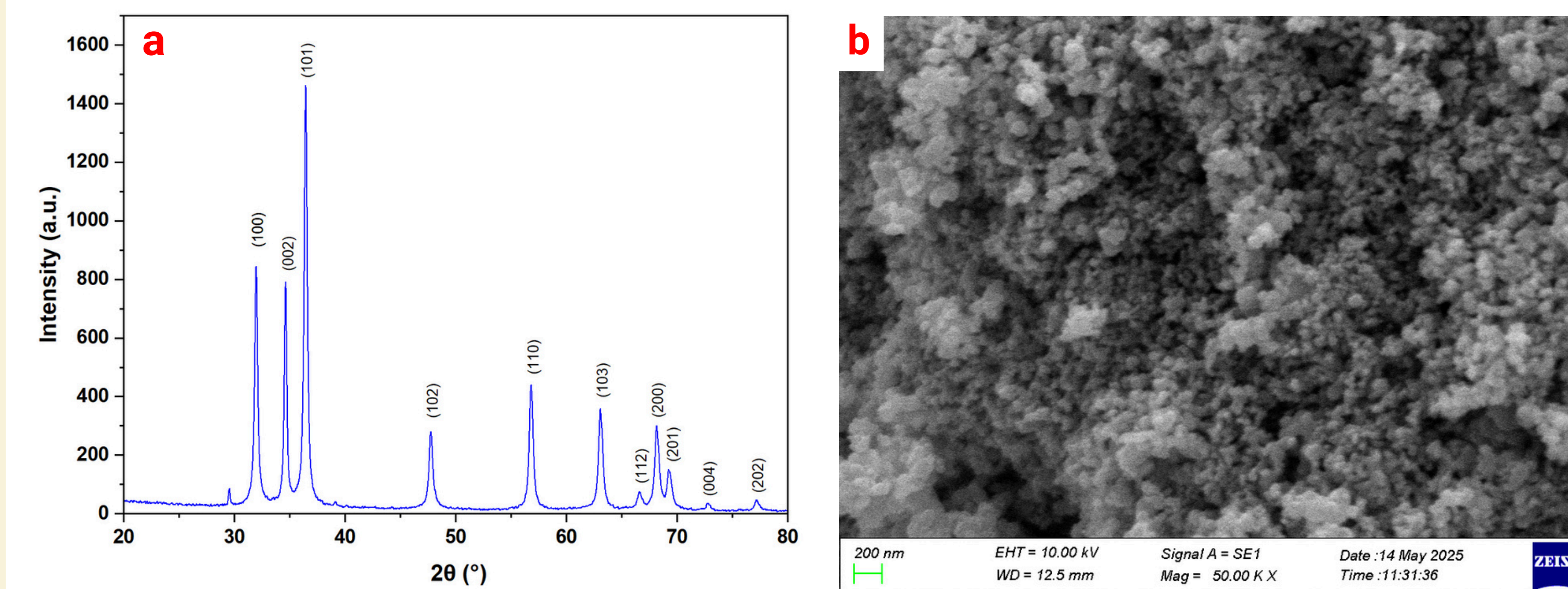


Figure 3: (a) PXRD pattern of ZnO NPs.

Figure 3: (b) SEM image of ZnO NPs.

Figure 3: (c) FT-IR spectra of synthesized DHPMs.

Compound	Aldehyde	Time (h)	Melting point (°C)		Yield (%)	ZnO NPs recovered (mg)
			Observed	Reported		
(A)	C_6H_5	8	205-208	210-212	69	41
(B)	$4\text{-Cl-C}_6\text{H}_5$	6	212-214	215-216	55	44
(C)	$4\text{-H}_3\text{CO-C}_6\text{H}_5$	5	204-206	204-206	58	45
(D)	$4\text{-HO-C}_6\text{H}_5$	8	228-230	226-228	63	46
(E)	$4\text{-O}_2\text{N-C}_6\text{H}_5$	8	209-212	205-207	81	45

Table 1: Catalytic performance of ZnO NPs in Biginelli reaction after one cycle.

Figure 3(a) shows the XRD pattern of the ZnO NPs, with diffraction peaks at 31.95°, 34.37°, 36.45°, 47.73°, 56.77°, 63.06°, 66.60°, 68.14°, 69.27°, 72.75°, and 77.19°, corresponding to the (100), (002), (101), (110), (103), (112), (200), (201), (004), and (202) planes matching with JCPDS Card 36-1451. Figure 3(b) shows the morphology of the ZnO NPs, revealing predominantly spherical particles as dispersed clusters. Table 1 illustrates that the corresponding Biginelli products were synthesized with yield and melting points in good accordance with literature.

The catalyst has thermal and chemical stability and is a sustainable, economical, environmentally friendly and recyclable catalyst. The advantages of this study are its simplicity, straightforward procedures, elimination of toxic reagents and homogeneous catalysts, elimination of synthetic surfactants and capping agent, the use of ethanol as a green solvent and moderate yields.

References

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- [2] Krishna, T.; Laxminarayana, E.; Kalita, D. FeF₃ as a Green Catalyst for the Synthesis of Dihydropyrimidines via Biginelli Reaction. *European Journal of Chemistry* **2020**, 11 (3), 206–212.