Supplementary Information

Insight into 6-Aminopenicillanic Acid Structure and Study of the Quantum Mechanical Calculations as the Acid-Base site onto γ-Fe_2O_3@SiO_2 Core-Shell Nanocomposites and Efficient Catalysts in Multicomponent Reactions

Farveh Saberi[a], Somayeh Ostovar*[a], Roya Behazin [a], Alireza Rezvani [a], Ali Ebrahimi [a] and Hamid Reza Shaterian [a]

[a]*Department of Chemistry, University of Sistan and Baluchestan, Faculty of Sciences, PO Box 98135-674, Zahedan, (Iran).*

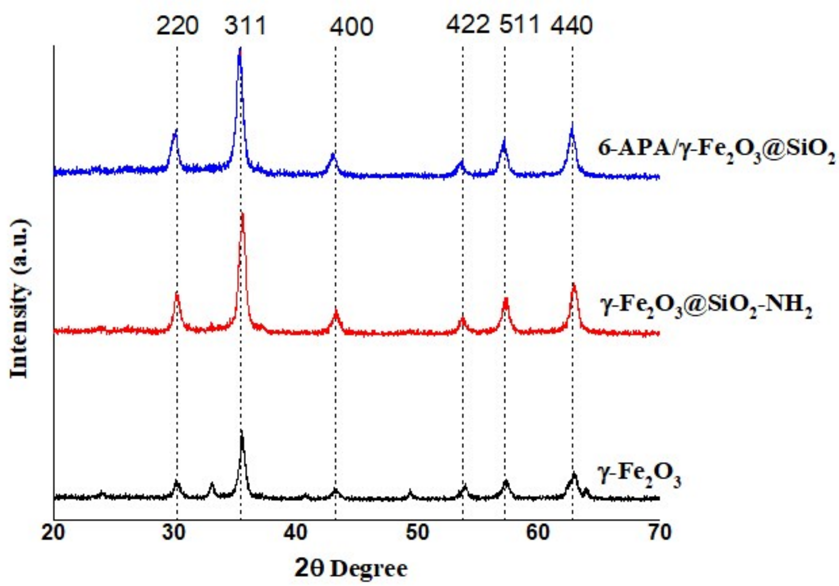


Fig. S1: XRD pattern of γ-Fe_2O_3, **γ-**Fe_2O_3@SiO_2 and 6-APA/**γ-**Fe_2O_3@SiO_2

Table S1. Elemental distribution (atomic %) of γ-Fe_2O_3/SiO_2-STZ.

Sample	Fe	O	Si	C	S	N	Total
6-APA/γ-Fe_2O_3@SiO_2	47	37.09	4.64	5.39	0.49	5.25	100

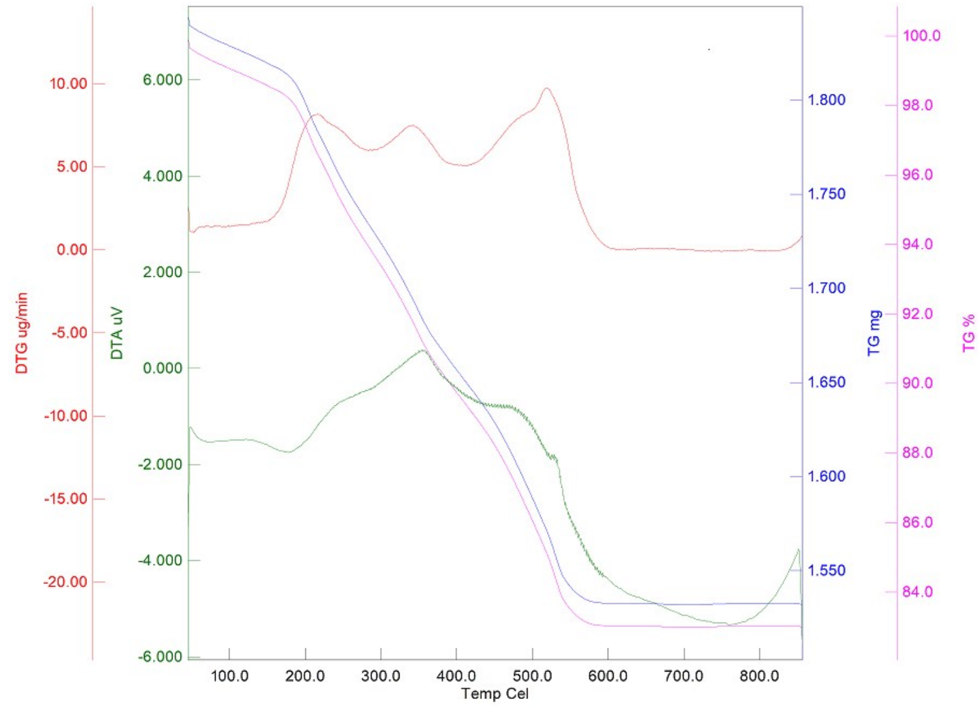


Fig. S2: Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of 6-APA/**γ-** Fe_2O_3@SiO_2

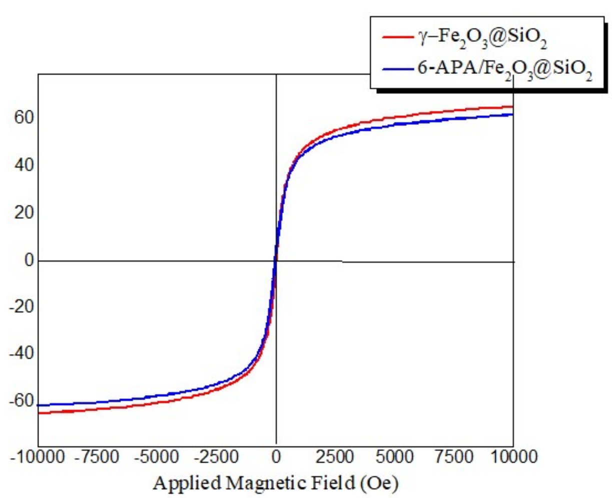


Fig. S3: VSM diagram of γ-Fe_2O_3@SiO2 and 6-APA/γ-Fe_2O_3@SiO_2

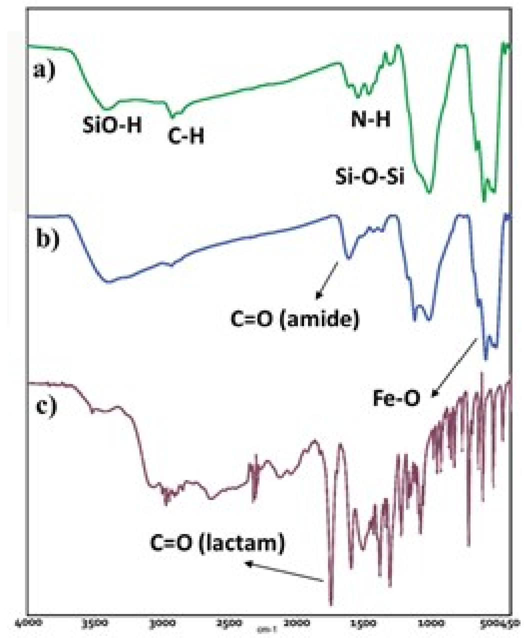
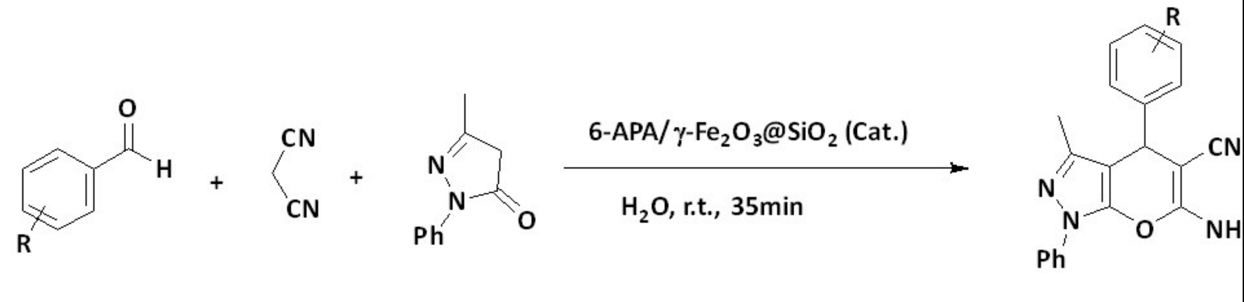
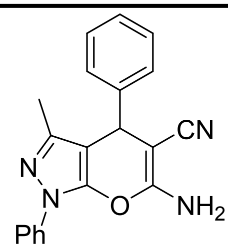
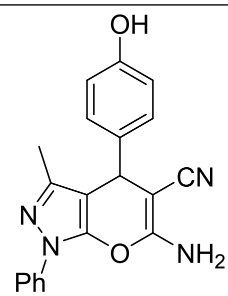
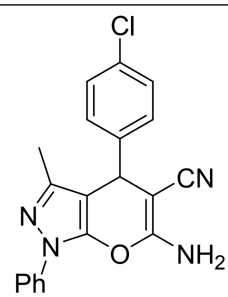
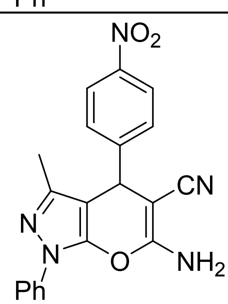
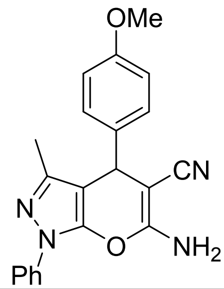
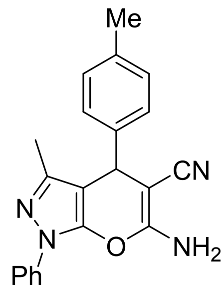
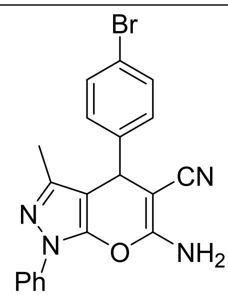
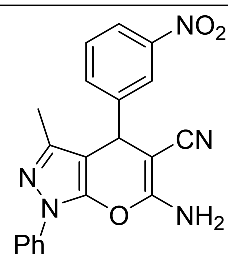
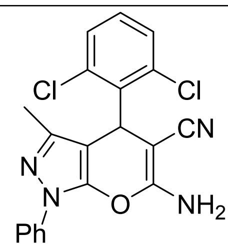
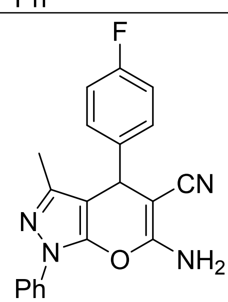


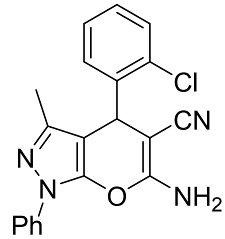
Fig. S4: FT-IR spectra of (a) **γ-**Fe_2O_3@SiO_2-NH_2, (b) 6-APA/**γ-**Fe_2O_3@SiO_2, and (c) 6-APA

Table S2. Study of multicomponent reaction of 1,4-dihydropyrano[2,3-c] pyrazole derivatives



Entrya	Aldehydes	Product	Time (min.)	Yieldb(%)	Melting Point ℃
1	Ph-		20	90	168-1701
2	4-OH-Ph-		25	89	210-2122
3	4-Cl-Ph-		15	94	175–1791
4	4-NO2-Ph-		10	96	192-1961

5	4-MeO-Ph-		30	86	172–1741
6	4-Me-Ph-		25	88	177–1791
7	4-Br-Ph-		10	95	176-1793
8	3-NO2-Ph-		20	91	187–1901
9	2,6-Cl-Ph-		15	92	180–1841
10	4-F-Ph-		15	94	166–1681

11	2-Cl-Ph-		15	92	144-1472

a Reaction conditions: aldehyde (2 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H) -one (2 mmol), malononitrile (2 mmol), catalyst (30 mg), H2O (4 ml), during 30 min at room temperature

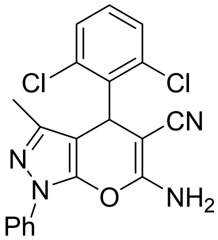
b Isolated yield

Table S3: Comparison of 6-APA/γ-Fe2O3@SiO2with other catalysts reported in the literature for the synthesis of 1,4-dihydropyrano [2,3-c] pyrazole

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref
1	OPC-SO3H (0.02gr)0	EtOH at 80℃	2	91	4
2	Fe3O4@THAM-SO3H (0.01gr)	EtOH-H2O(1:1), reflux	10	80	5
3	NB-Fe3O4@SiO2@CPTMO@DEA-SO3H	EtOH-H2O(2:1), reflux	40	93	6
4	Fe3O4@GO-N-(pyridin-4-amine) (0.01gr)	H2O, reflux	30	94	8
5	6-APA/γ-Fe2O3@SiO2 (0.03gr)	H2O, rt	20	90	Present work

Analytical data for selected compound:

6-Amino-4-(2,6-dichlorophenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c] pyrazole



White powder. Melting point = 180-184℃. Yield: 92%.

[1] H NMR (300 MHz, DMSO-d6): δ = 1.793 (s, 3H, CH3), 5.678 (s, 1H, 4-H), 7.314–7.782 (m, 7H, ArH), 7.807-7811 (d, 2H, ArH).

IR (KBr) νmax: 3456, 3321, 2198, 1660, 1591, 1392, 1269, 1126, 1049, 758 cm^{-1}.

References

1. S. R. Mandha, S. Siliveri, M. Alla, V. R. Bommena, M. R. Bommineni and S. Balasubramanian, *Bioorganic & medicinal chemistry letters*, 2012, **22**, 5272-5278.
2. T. S. Jin, A. Q. Wang, Z. L. Cheng, J. S. Zhang and T. S. Li, *Synthetic communications*, 2005, **35**, 137-143.
3. S. B. Guo, S. X. Wang and J. T. Li, *Synthetic Communications*, 2007, **37**, 2111-2120.
4. N. Nagasundaram, M. Kokila, P. Sivaguru, R. Santhosh and A. Lalitha, *Advanced Powder Technology*, 2020.
5. H. Faroughi Niya, N. Hazeri and M. T. Maghsoodlou, *Applied Organometallic Chemistry*, 2020, **34**, e5472.
6. B. Eftekhari far and M. Nasr-Esfahani, *Applied Organometallic Chemistry*, 2020, **34**, e5406.
7. H. Ghafuri, M. Kazemnezhad Leili and H. R. Esmaili Zand, *Applied Organometallic Chemistry*, 2020, e5757.
8. D. Azarifar and M. Khaleghi-Abbasabadi, *Research on Chemical Intermediates*, 2019, **45**, 199-222.