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Synthesis of novel magnetic nanoparticles with urea or urethane moieties: Applications as catalysts in the Strecker synthesis of α -aminonitriles

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Four novel magnetic nanoparticle catalysts with urea or urethane moieties are reported. The silica-coated magnetic nanoparticles were simply functionalized via addition of 3-(triethoxysilyl)propylisocyanate (TESPIC), amine or amino alcohol. TESPIC with dual labile functional groups was used as a suitable precursor for the synthesis of urethane-based catalysts. The newly synthesized catalysts were fully characterized using a variety of techniques. These functionalized magnetic nanoparticles were used as reusable catalysts in the Strecker synthesis of α -aminonitrile derivatives under solvent-free conditions at 50 °C.

KEYWORDS

3-(triethoxysilyl)propylisocyanate, magnetic nanoparticle, Strecker synthesis, urea or urethane moiety, α -aminonitrile

1 | INTRODUCTION

With the development of self-assembly processes, functional self-assembled materials have attracted more and more attention. 3-(Triethoxysilyl)propylisocyanate (TESPIC) with dual labile functional groups has been widely used as a reagent, the structure of which includes isocyanate ($-\text{N}=\text{C}=\text{O}$) and ethoxy ($-\text{O}-\text{CH}_2-\text{CH}_3$) functional groups. Because of the high reactivity of these functional groups, TESPIC has been used as a crosslinking reagent in various addition reactions. Recent developments of using TESPIC in assembling hybrid materials and in the synthesis of novel compounds have also been reported.^[1] The internal ester group of isocyanate in the TESPIC molecule is expected to realize hydrogen transfer reaction with some active molecules having reactive hydrogen atoms.^[2]

Urea and urethane derivatives are significant types of carbonyl compounds that can be used in a wide variety of applications. They have found uses as antioxidants in gasoline, as additives in the synthesis of amino-plastics, as plant protecting agents and in pharmaceutical and dye chemistry.^[3] Special attention has recently been paid to urea derivatives since a number of them have been used for brain cancer treatment, or have been confirmed to have a marked inhibitory effect on HIV protease enzyme.^[4] These compounds are produced using several methods such as the reaction between amine derivatives and compounds like isocyanates, carbamates and formamides in the presence of transition metal catalysts like Ru, Ni, Co, Pd, Au and W.^[5]

Bifunctional organo-catalysts bearing both urea/thio-urea hydrogen-bond donors and a basic amine moiety

have been reported as practical organo-catalysts for asymmetric transformations.^[6] Takemoto and co-workers^[7] showed that the introduction of a basic group in a thiourea catalyst leads to a synergistic interaction between the functional groups in substrates. They reported that bifunctional amine–thiourea organo compounds are efficient catalysts in enantioselective Michael addition reactions. Such a catalyst has been used in a wide range of organic transformations.^[8]

Nanoparticles of catalytic material provide the benefit of high surface area that leads to an increased reaction rate. Magnetic nanoparticles (MNPs) have been widely studied as a support for catalysts because there is an extensive interest in the attachment of various catalyst molecules onto heterogeneous substrates.^[9] They are valuable substrates for the immobilization of inorganic and organic catalysts. Advantages are the easy separation from the reaction mixture and recycling of the catalyst by a simple magnetic separation.^[10]

The Strecker reaction is a simple and efficient one-pot three-component method for the preparation of α -aminonitriles, which employs aldehydes or ketones, amines and a cyanide source in aqueous media.^[11] α -Aminonitriles are valuable intermediates in the synthesis of α -amino acids and other biologically relevant molecules.^[12] They have also been investigated for their role in the chemistry and prebiotic evolution of α -amino acids.^[13] The Strecker synthesis has been widely extended using numerous catalysts.^[14]

In continuation of our research in the area of developing silica-coated magnetic iron oxide nanoparticles with various coating systems and their applications as catalysts in multicomponent reactions,^[15] herein we describe the synthesis and characterization of four types of novel MNPs functionalized with urea or urethane moieties (Schemes 1 and 2). Then, the activity of these heterogeneous catalysts was investigated in the Strecker synthesis of α -aminonitrile derivatives by the reaction between trimethylsilyl cyanide (TMSCN), various aldehydes or ketones, and amines under solvent-free conditions at 50 °C (Scheme 3).

All the synthesized novel compounds containing urea or urethane moieties (i.e. **6**, **7**, **8** and **9** in Scheme 1) were fully identified and characterized using FT-IR, ¹H NMR, ¹³C NMR and HRMS (refer to supporting information). The MNPs functionalized with these new silane compounds (i.e. **10a–d** in Scheme 2) were also fully characterized via FT-IR, TGA, DTG, DTA, DSC, XRD, TEM, BET, AFM, XPS and VSM analyses (refer to supporting information). Development of design and synthesis of functionalized MNP catalysts for multicomponent reactions^[16] was our main purpose because these catalytic systems play a major role in organic functional group transformations. With this purpose, **10a–d** were used as efficient and recyclable catalysts for the Strecker synthesis of

SCHEME 1 Synthesis of novel compounds with urea or urethane moieties using TESPIC as an efficient precursor

SCHEME 2 Synthesis of novel MNP catalysts with urea or urethane moieties using TESPIC as an efficient precursor

α -aminonitrile derivatives. This was achieved by reacting various aldehydes or ketones, TMSCN and amine derivatives under solvent-free conditions at 50 °C (Scheme 3).

2 | RESULTS AND DISCUSSION

The Strecker synthesis of α -aminonitrile derivatives via the reaction between 4-nitrobenzaldehyde, aniline and TMSCN was chosen as a model reaction and the influence of the synthesized nanocatalysts (**10a–d**) on the yield and reaction time was investigated (Table 1). In the absence of **10a–d** no product was obtained at room temperature (Table 1, entry 1). By increasing the reaction temperature to 50 °C, the product was synthesized with

SCHEME 3 Strecker synthesis of α -aminonitrile derivatives using the new MNP catalysts with urea or urethane moieties

an isolated yield of 15%. This implies that the use of catalyst is inevitable for this transformation. To determine the optimal reaction conditions, optimization of the amount of catalyst, temperature and solvent was carried out. The catalyst quantity was optimized to achieve the maximum catalytic activity and all the preliminary experiments were done under solvent-free condition. The results given in Table 1 reveal that 1 mg of catalyst at 50 °C (entry 7) gave the best yield which is equivalent to the case of using twice as much catalyst at room temperature (entry 17). There was no important modification in the yield of product when large amounts of MNP catalysts were used instead of 1 mg (Table 1, entries 18 and 20). Further increasing the temperature to 100 °C and catalyst quantity up to 5 mg did not have a pronounced influence on the yield.

Various solvents, namely water, C_2H_5OH , CH_3CN , CH_2Cl_2 , *n*-hexane, CH_3CO_2Et and toluene, were also investigated. As evident from Table 1 (entries 10–16), the model reaction in solvents either takes more time or proceeds in lower yield compared to the solvent-free condition.

TABLE 1 Optimization of reaction conditions in synthesis of 2-(4-nitrophenyl)-2-(phenylamino)acetonitrile^a

Entry	Catalyst amount (mg)	Reaction temperature (°C)	Solvent	Reaction time (min)	Yield (%) ^b			
					10a	10b	10c	10d
1	—	r.t.	—	60	—	—	—	—
2	—	50	—	60	15	15	15	15
3	0.5	r.t.	—	60	35	28	30	33
4	0.5	50	—	60	53	41	46	52
5	0.5	100	—	60	53	41	46	52
6	1	r.t.	—	30	71	63	65	69
7	1	50	—	15	93	85	88	90
8	1	75	—	15	93	85	88	90
9	1	100	—	15	93	85	88	90
10	1	50	H ₂ O	30	78	68	70	74
11	1	50	C ₂ H ₅ OH	15	91	82	85	88
12	1	50	CH ₃ CN	15	88	78	80	83
13	1	50	CH ₂ Cl ₂	30	83	76	79	81
14	1	50	<i>n</i> -hexane	60	73	62	64	69
15	1	50	CH ₃ CO ₂ Et	30	81	73	75	77
16	1	50	Toluene	60	74	65	67	71
17	2	r.t.	—	30	71	63	65	69
18	2	50	—	15	93	85	88	90
19	5	r.t.	—	30	68	61	63	65
20	5	50	—	15	91	83	85	87

^aReaction conditions: 4-nitrobenzaldehyde (1 mmol; 0.151 g), TMS-CN (1.5 mmol; 0.149 g; 0.188 ml), aniline (1 mmol; 0.093 g; 0.092 ml).

^bIsolated yield.

TABLE 2 Strecker synthesis of α -aminonitrile derivatives catalysed by **10a–d** under solvent-free conditions at 50°C^a

Entry	Product	M.p. (°C) (colour)	Time (min)	Yield (%) ^b			
				10a	10b	10c	10d
1		110–112 (yellow solid)[^{16a}]	20	91	83	86	88
2		215–217 (yellow solid)[^{16b}]	15	93	85	88	90
3		31–33 (red solid)[^{17a}]	15	93	85	88	90
4		85–87 (red solid)[^{17a}]	10	95	87	90	92
5		111–113 (brown solid)[^{17a}]	20	91	83	86	88
6		88–90 (brown solid)[^{17b}]	15	93	85	88	90
7		71–73 (green solid)[^{17a}]	25	89	81	84	86
8		104–106 (green solid)[^{17a}]	20	91	83	86	88
9		158–160 (yellow solid)[^{17c}]	30	87	80	82	84
10		103–105 (red solid)[^{17d}]	25	89	81	84	86
11		82–84 (green solid)[^{17a}]	30	87	80	82	84

(Continues)

TABLE 2 (Continued)

Entry	Product	M.p. (°C) (colour)	Time (min)	Yield (%) ^b			
				10a	10b	10c	10d
12		103–105 (green solid)[^{17a}]	25	89	81	84	86
13		Yellow oil[^{17e}]	25	92	81	85	86
14		Yellow oil[^{17e}]	25	93	84	87	89
15		Yellow oil[^{17e}]	25	94	85	87	90
16		71–73 (yellow solid)[^{17e}]	25	91	81	83	87
17		Yellow oil[^{17e}]	30	90	79	82	83
18		Yellow oil[^{17e}]	30	91	82	85	87
19		120–122 (yellow solid)[^{17e}]	30	85	78	80	81
20		Yellow oil[^{17e}]	30	83	80	82	84

(Continues)

TABLE 2 (Continued)

Entry	Product	M.p. (°C) (colour)	Time (min)	Yield (%) ^b			
				10a	10b	10c	10d
21		134–136 (yellow solid)[^{17c}]	30	89	77	79	81
22		54–56 (yellow solid)[^{17c}]	30	90	78	81	83
23		Yellow oil[^{17b}]	30	85	83	84	86
24		57–59 (white solid)[^{17f}]	30	84	81	82	85

^aReaction conditions: aldehyde or ketone (1 mmol), TMSCN (1.5 mmol; 0.149 g; 0.188 ml), amine derivatives (1 mmol).

^bIsolated yield.

Under the optimized reaction conditions, various α -aminonitrile derivatives were prepared through Strecker

synthesis catalysed by our heterogeneous bifunctional organo-catalysts. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted effectively and provided the products in high to excellent yields. It was found that aromatic aldehydes with electron-withdrawing groups reacted faster than those with electron-donating groups. Also aromatic aldehydes reacted faster than aliphatic aldehydes and ketones. The data in Table 2 show that aliphatic amines

TABLE 3 Reusability of 10a–d in synthesis of 2-(4-nitrophenyl)-2-(phenylamino)acetonitrile in 15 min^a

Run	Yield (%) ^b			
	10a	10b	10c	10d
1	93	85	88	90
2	93	85	88	90
3	93	84	87	89
4	92	84	87	89
5	92	83	87	88
6	91	83	86	88
7	91	82	86	87

^aReaction conditions: 4-nitrobenzaldehyde (1 mmol; 0.151 g), TMSCN (1.5 mmol; 0.149 g; 0.188 ml), aniline (1 mmol; 0.093 g; 0.092 ml).

^bIsolated yield.

SCHEME 4 Plausible mechanism for Strecker synthesis of α -aminonitriles catalysed by 10d

TABLE 4 Comparison of catalytic efficacy of MNP catalysts with other catalysts^a

Entry	Catalyst/amount	Conditions	Time (min)	Yield (%) ^b
1	10a /1 mg	Solvent-free, 50 °C	20	91
2	10b /1 mg	Solvent-free, 50 °C	20	83
3	10c /1 mg	Solvent-free, 50 °C	20	86
4	10d /1 mg	Solvent-free, 50 °C	20	88
5	B-MCM-41/50 mg	EtOH, r.t.	90	98 ^[17b]
6	Choline chloride.2ZnCl ₂	Solvent-free, r.t.	1.3	99 ^[17d]
7	Chitosan/6 mg	Solvent-free, r.t.	3	95 ^[17a]
8	Ga-TUD/20 mg	Solvent-free, r.t.	30	92 ^[19a]
9	PVP-SO ₂ /100 mg	CH ₂ Cl ₂ , 50 °C	360	89 ^[19b]
10	PEG-OSO ₃ H/180 mg	H ₂ O, r.t.	10	92 ^[17f]
11	Sn-montmorillonite/10 mg	Solvent-free, r.t.	6	90 ^[19c]
12	MCM-41-SO ₃ H/5 mg	EtOH, r.t.	30	98 ^[19d]
13	<i>p</i> -TSA/10 mol%	EtOH, r.t.	15	87 ^[16a]
14	Zr(HSO ₄) ₄ /2–6 mol%	Solvent-free, r.t.	10	85 ^[17c]
15	K ₂ PdCl ₄ /10 mol%	H ₂ O, r.t.	30	91 ^[19e]
16	I ₂ /51 mg	CH ₃ CN, r.t.	60	90 ^[19f]

^aReaction conditions: 4-chlorobenzaldehyde (1 mmol; 0.140 g), TMSCN (1.5 mmol; 0.149 g; 0.188 ml), aniline (1 mmol; 0.093 g; 0.092 ml).^bIsolated yield.

have shorter reaction time and afford higher yields of products than aromatic amines. This is because the electron pair in aliphatic amines is not in resonance with any functional groups and aromatic rings, so these compounds have a more nucleophilic property and can attack carbonyl compounds faster than can aromatic amines.

The possible mechanism of the Strecker reaction begins with the activation of the carbonyl group of the aldehyde or ketone (**11**) by the —NH amide groups of the catalysts (**10d** is shown in Scheme 4 as an example) via hydrogen bonding. This makes the nucleophilic attack of the amine (**13**) on the carbonyl group to produce the corresponding imine (**16**) more favoured. Water removal from the intermediate (**15**) can also be considered as a driving force for imine formation. In the next step, the —NH amide groups of **10d** can further activate imine nitrogen through hydrogen bonding and at the same time the silicon atom in TMSCN can be coordinated by the lone pair electrons of the pyridine nitrogen atom of the catalyst. The imine is then attacked by the cyanide group of TMSCN to provide the desired α -aminonitrile derivative.^[18]

As the recyclability of a heterogeneous catalyst is a significant factor, we investigated the recyclability and reusability of all the newly synthesized catalysts on repeated use in the model reaction. After the reaction was completed (monitored by TLC) the catalyst was separated simply using an external magnet, washed with ethanol and reused for the next run (seven times). The yield of the product and reaction time remained unchanged after seven cycles, indicating that the

catalysts are fully recyclable and reusable for several runs preserving the catalytic activity (Table 3).

To investigate the efficacy of the synthesized MNPs with urea or urethane moieties as catalysts for the Strecker synthesis, we compared the results obtained in this work with those reported in the literature for Strecker reaction mediated by other catalysts (Table 4). It is clear that our new MNP urethane catalysts (**10a–d**) efficiently catalyse the Strecker reaction. The new catalysts are comparable in some cases with those previously reported for Strecker synthesis and in some cases are superior. The greatest advantages of the present catalysts in comparison to previously reported ones are high surface area, easy separation, Takemoto catalyst-like nature, short reaction time and mild and solvent-free conditions that make this method from the green chemistry point of view more environmentally friendly.

3 | CONCLUSIONS

In summary, we have developed a novel and facile process for the synthesis of Fe₃O₄@SiO₂@urea and Fe₃O₄@SiO₂@urethane catalysts using TESPIC as an efficient precursor. These easily recyclable catalysts were used efficiently for one-pot multicomponent synthesis of α -aminonitriles in Strecker reaction using numerous aldehydes or ketones, TMSCN and amines under solvent-free

conditions at 50 °C. Due to the integrative combination of various advantages such as facile synthesis, ease of recovery and solvent-free reaction conditions, the protocol presented can be considered as an environmentally benign approach for synthesizing α -aminonitriles via the Strecker reaction. This investigation can open up a new insight into the course of design, synthesis and applications of urea or urethane fertilizer-based MNP catalysts for sustainable methods.

4 | EXPERIMENTAL

4.1 | General procedure for synthesis of compounds with urea or urethane moieties (6–9)

TESPIC (5 mmol; 1.237 g; 1.238 ml) was added to substrates **2** to **5** (5 mmol) in a round-bottom flask and the resulting mixture was stirred for 30 min at 50 °C (Scheme 1). After completion of the reaction, the resulting mixture was washed repeatedly with diethyl ether (10 ml) to remove any unreacted starting materials and to obtain the highest possible purity. The resulting viscous liquids were then dried under vacuum at 50 °C for 30 min. All the synthesized compound **6–9** were identified using FT-IR, ^1H NMR, ^{13}C NMR and HRMS (refer to supporting information; Figures S1–S24).

4.1.1 | N^1, N^4 -Bis(3-(triethoxysilyl)propyl)piperazine-1,4-dicarboxamide (6)

Yellow viscous liquid; yield 95%. IR (KBr, ν , cm^{-1}): 3379, 2982, 2968, 2918, 1638, 1548, 1396, 1259, 1114, 1107, 962, 796. ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 6.49 (s, 1H, $-\text{NH}$), 4.32 (t, $J = 4.9$ Hz, 2H, $\text{H}-\text{C}_3$), 3.71 (q, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_6$), 3.42 (t, $J = 4.9$ Hz, 2H, $\text{H}-\text{C}_5$), 3.20 (s, 4H, $\text{H}-\text{C}_1$), 2.96 (q, $J = 7.0$ Hz, 2H, $\text{H}-\text{C}_4$), 1.12 (t, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_7$), 1.04 (t, $J = 7.0$ Hz, 3H, $\text{H}-\text{C}_7$). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 160.4 (C_2), 60.7 (C_1), 59.1 (C_3), 46.2 (C_6), 46.0 (C_5), 21.6 (C_4), 21.3 (C_7). HRMS (ESI/TOF-Q) m/z : $[\text{M} + \text{H}]^+$. Calcd for $\text{C}_{24}\text{H}_{53}\text{O}_8\text{N}_4\text{Si}_2$: 581.33988; found: 581.33964.

4.1.2 | Nitrilotris(ethane-2,1-diyl)tris((3-(triethoxysilyl)propyl)carbamate) (7)

Yellow viscous liquid; yield 94%. IR (KBr, ν , cm^{-1}): 3370, 3237, 3090, 2979, 2932, 2915, 1692, 1598, 1483, 1417, 1306, 1109, 1105, 961, 781. ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 7.02 (s, 1H, $-\text{NH}$), 3.71 (q, $J = 6.9$ Hz, 6H, $\text{H}-\text{C}_7$), 3.39 (dd, $J = 16.6, 6.7$ Hz, 4H, $\text{H}-\text{C}_1$ and $\text{H}-\text{C}_2$), 2.91 (q, $J = 6.1$ Hz, 2H, $\text{H}-\text{C}_5$), 1.42 (t, $J = 7.0$ Hz, 2H, $\text{H}-\text{C}_4$), 1.12 (t, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_8$), 1.04 (t, $J = 7.0$ Hz, 5H, $\text{H}-\text{C}_6$ and $\text{H}-\text{C}_8$). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 166.8 (C_3), 62.8 (C_1), 48.3 (C_4), 46.2 (C_2), 38.9 (C_7), 27.8 (C_6), 23.8 (C_5), 17.1 (C_8). HRMS (ESI/TOF-Q) m/z : $[\text{M} + \text{H}]^+$. Calcd for $\text{C}_{36}\text{H}_{79}\text{O}_{15}\text{N}_4\text{Si}_3$: 891.48492; found: 891.48442.

4.1.3 | 1-(Pyridin-2-yl)-3-(3-(triethoxysilyl)propyl)urea (8)

Orange viscous liquid; yield 96%. IR (KBr, ν , cm^{-1}): 3377, 3245, 2978, 1691, 1590, 1484, 1108, 1105, 964, 781. ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 9.15 (s, 1H, $-\text{NH}$), 8.24 (s, 1H, $-\text{NH}$), 8.12 (d, $J = 4.2$ Hz, 1H, $\text{H}-\text{C}_1$), 7.62 (t, $J = 7.8$ Hz, 1H, $\text{H}-\text{C}_2$), 7.31 (d, $J = 8.4$ Hz, 1H, $\text{H}-\text{C}_3$), 6.86 (t, $J = 6.8$ Hz, 1H, $\text{H}-\text{C}_4$), 3.71 (q, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_{10}$), 3.43 (q, $J = 7.0$ Hz, 1H, $\text{H}-\text{C}_8$), 3.14 (q, $J = 7.0$ Hz, 1H, $\text{H}-\text{C}_8$), 1.51 (t, $J = 7.2$ Hz, 2H, $\text{H}-\text{C}_7$), 1.11 (t, $J = 7.0$ Hz, 6H, $-\text{H}-\text{C}_{11}$), 1.04 (t, $J = 7.0$ Hz, 5H, $\text{H}-\text{C}_9$ and $\text{H}-\text{C}_{11}$). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 157.8 (C_6), 156.6 (C_5), 149.6 (C_1), 141.1 (C_2), 119.6 (C_4), 114.6 (C_3), 60.7 (C_7), 59.1 (C_{10}), 44.6 (C_9), 26.3 (C_8), 21.2 (C_{11}). HRMS (ESI/TOF-Q) m/z : $[\text{M} + \text{H}]^+$. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_4\text{N}_3\text{Si}$: 342.18428; found: 342.18436.

4.1.4 | 1-(Pyridin-4-yl)-3-(3-(triethoxysilyl)propyl)urea (9)

Red viscous liquid; yield 97%. IR (KBr, ν , cm^{-1}): 3407, 3314, 2986, 1712, 1600, 1554, 1213, 1111, 1087, 828. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.85 (s, 1H, $-\text{NH}$), 8.30 (dd, $J = 33.5$, 5.8 Hz, 2H, $\text{H}-\text{C}_3$), 7.40 (dd, $J = 30.2$, 5.9 Hz, 2H, $\text{H}-\text{C}_2$), 4.38 (s, 1H, $-\text{NH}$), 3.73 (t, $J = 7.0$ Hz, 2H, $\text{H}-\text{C}_5$), 3.68 (t, $J = 7.0$ Hz, 2H, $\text{H}-\text{C}_7$), 3.43 (q, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_8$), 3.06 (q, $J = 7.0$ Hz, 2H, $\text{H}-\text{C}_6$), 1.12 (t, $J = 7.0$ Hz, 6H, $\text{H}-\text{C}_9$), 1.04 (t, $J = 7.0$ Hz, 3H, $\text{H}-\text{C}_9$). ^{13}C NMR (101 MHz, DMSO , δ , ppm): 157.6 (C_4), 153.2 (C_1), 152.9 (C_3), 151.9 (C_2), 60.7 (C_5), 59.1 (C_8), 44.8 (C_7), 21.5 (C_6), 21.2 (C_9). HRMS (ESI/TOF-Q) m/z : $[\text{M} + \text{H}]^+$. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_4\text{N}_3\text{Si}$: 342.18439; found: 342.18436.

4.2 | General procedure for synthesis of MNP compounds with urea or urethane moieties (10a–10d).

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell MNPs were synthesized according to a previously reported procedure.^[20] $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell MNPs (0.2 g) were homogeneously dispersed by ultrasonic vibration in 50 ml of dry ethanol. Then, each compound **6** to **9** in Scheme 2 (1 mmol) was added to the resulting mixture and stirred for 24 h under nitrogen atmosphere reflux condition. After completion of the reaction, the resulting mixture was washed repeatedly with a mixture of ethanol and deionized water (10:1) to remove any unreacted starting materials in order to achieve high purity, and then was dried under vacuum at 80 °C for 24 h. Each compound **10a–d** was identified by FT-IR, TGA, DTG, DTA, DSC, XRD, TEM, BET, AFM, XPS and VSM analyses (refer to supporting information; Figures S25–S60, Tables S1–S4).

4.3 | General procedure for Strecker synthesis of α -Aminonitrile derivatives using 10a–d as MNP catalysts

Compounds **10a–d** as MNP catalysts (1 mg) were added to a mixture of aldehydes or ketones (1 mmol), TMSCN

(1.5 mmol; 0.149 g; 0.188 ml) and amine derivatives (1 mmol) under solvent-free conditions at 50 °C. The progress of the reaction was monitored by TLC (n -hexane–ethyl acetate, 5:2). At the end of the reaction, the product was washed with ethanol and the catalyst was separated using an external magnet (the products are soluble in ethanol). The recycled catalyst was used in the next run of the model reaction without significant loss of activity. The solvent of the organic layer was removed and the crude product was purified using a short column of silica gel (n -hexane–ethyl acetate, 20:1) to yield pure products.

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