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Efficient and selective Copper-grafted nanoporous silica in aqueous conversion of aldehydes to amides

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Functionalization of the SBA-15 to NH_2-SBA-15/Cu:

The calcinated SBA-15 (1 g) will react with 100 mL of 0.01 M solution of (3-aminopropyl)triethoxysilane in dry toluene under reflux condition for 10 h. The product was filtered, and then dried under vacuum. CHN analysis for loading of nitrogen showed 0.62%. Complexation of the amine-modified SBA-15 (NH_2-SBA-15) with copper is similar to preparation of the SBA-15/En-Cu. In a typical synthesis, 1 g of NH_2-SBA-15 was activated at 60 ℃ for 5 h. and then was dispersed in MeOH/H_2O (25 mL:25 mL). In other pot 1 mmol of copper acetate was dissolved in 10 ml H_2O and it was added into the previously prepared NH_2-SBA-15 dispersion dropwise and it was stirred at room temperature for 24 h. The solvent was removed by

filtration, and the resulting solid was washed with copious H_2O (×2 with 5 min bath sonication) and ethanol and finally with dichloromethane several times, and dried in oven vacuum over 60 °C.

Figure 1. Synthesized NH_2-SBA-15/Cu (a) and SB-15/En-Cu (b).

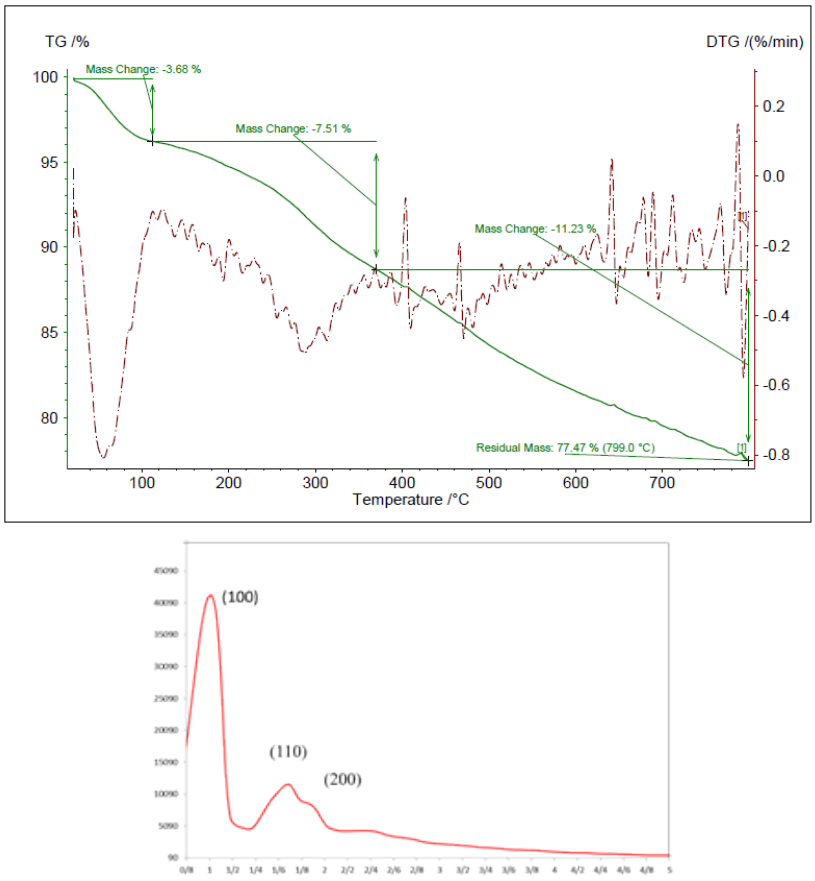
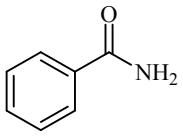


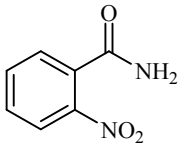
Figure 2. TG analysis and XRD pattern of SB-15/En-Cu.

Benzamide:



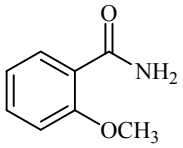
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.01 (1 H, s, 1H of NH), 7.88 (2 H, m, 2 H of CH aromatic), 7.54 (1 H, m, 1 H of CH aromatic), 7.46 (2 H, m, 2H of CH aromatic), 7.39 (1 H, s, 1H of NH); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 168.41 ($\underline{C}ONH_2$), 134.65 ($_{Ar}\underline{C}CONH_2$), 131.73 ($_{para}CH$), 128.69 ($_{ortho}CH$), 127.91 ($_{meta}CH$).

2-Nitrobenzamide:



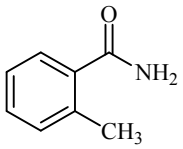
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (1 H, s, 1H of NH), 8.00 (1 H, d, 1 H of CH aromatic $^{3}J_{HH}$ = 8.0 Hz), 7.78 (1 H, t, 1 H of CH aromatic, $^{3}J_{HH}$ = 7.6 Hz), 7.72 (1 H, s, 1 H of NH), 7.70-7.64 (2 H, m, 2 H of CH aromatic); ^{13}C NMR (100 MHz; DMSO-d_6): δ =167.65 ($\underline{C}ONH_2$), 147.7 ($_{Ar}\underline{C}CONH_2$), 133.83 ($_{meta}\underline{C}$), 132.98 ($_{Ar}\underline{C}NO_2$), 131.12 ($_{meta}\underline{C}$), 129 .32 ($_{Ar}CH$),124.42 ($_{Ar}CH$).

2-Methoxybenzamide:



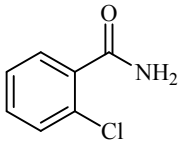
^{1}H NMR (400 MHz, DMSO-d_6): 7.81 (1 H, d, 1 H of CH aromatic, $^{3}J_{HH}$ = 7.6 Hz), 7.66 (1 H, s, 1 H of NH_2), 7.53 (1 H, s, 1 H of NH_2), 7.48 (1 H, t, 1 H of CH aromatic), 7.14 (1 H, d, 1 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 7.03 (1 H, t, , 1 H of CH aromatic , $^{3}J_{HH}$ = Hz), 3.89 (3 H, s, 3 H of OCH_3); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 166.76 ($\underline{C}ONH_2$), 157.70 ($_{Ar}\underline{C}CONH_2$), 132.98 ($_{meta}\underline{C}$),131.19 ($_{para}\underline{C}$), 123.02 ($_{Ar}\underline{C}OCH_3$), 120.87 ($_{Ar}CH$), 112.43 ($_{Ar}CH$), 56.26 ($O\underline{C}H_3$).

2- Methylbenzamide:



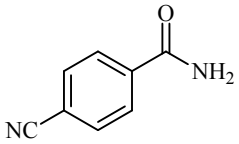
^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.93 (1 H, s, 1 H of NH), 7.78 (2 H, dd, 2 H of CH aromatic, $^{3}J_{HH}$ = 6.6 Hz), 7.29 (1 H, s, 1 H of NH), 7.25 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.0 Hz), 2.35 (3 H, s, 3 H of CH_3); ^{13}C NMR (100 MHz; DMSO-d_6): δ =168.26 ($\underline{C}ONH_2$), 141.58 ($_{Ar}\underline{C}CONH_2$), 131.86 ($\underline{C}CH_3$), 131.83 ($_{Ar}CH$), 129.22 ($_{Ar}CH$), 127.97 ($_{Ar}CH$), 21.41(CH_3).

2- Chlorobenzamide:



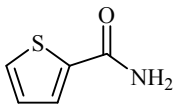
^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.90 (1 H, s, 1 H of NH), 7.61 (1 H, s, 1 H of NH),7.50-7.36 (4 H, m, 4 H of CH aromatic); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.60 ($\underline{C}ONH_2$), 137.51 ($_{Ar}\underline{C}CONH_2$), 131.07 ($_{Ar}\underline{C}Cl$), 130.08 ($_{Ar}CH$), 129.13 ($_{Ar}CH$), 129.13 ($_{Ar}CH$), 127.5 ($_{Ar}CH$).

4- Cyanobenzamide:



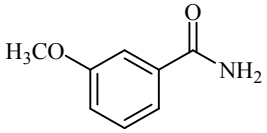
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.26 (1 H, s, 1 H of N$\underline{H}$), 8.03 (1 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4), 7.96 (1 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4), 7.7 (1 H, s, 1 H of NH); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 166.91 ($\underline{C}ONH2$), 138.70, 133.70 ($_{meta}C$), 132.87, 129.84, 128.68.

2-Thiophenecarboxamide:



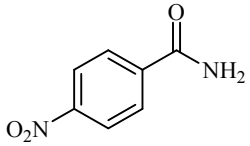
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.00 (1 H, s, 1 H of NH), 7.75-7.74 (2 H, m, 2 H of CH aromatic), 7.40 (1 H, s, 1H of NH), 7.14 (1 H, t, 1 H of CH aromatic, $^{3}J_{HH}$ = 4.2 Hz); ^{13}C NMR (100 MHz; DMSO-d_6): d= 163.3 ($\underline{C}ONH_2$), 140.68 ($_{Ar}\underline{C}CONH_2$), 131.47 ($_{Ar}CH$), 129.19 ($_{Ar}CH$), 128.39 ($_{Ar}CH$).

3-Methoxybenzamide:



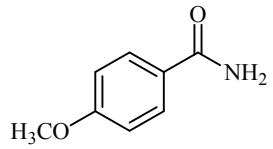
^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.80 (3 H, s, 3 H of OCH_3), 7.99 (1 H, s, 1 H of NH), 7.47-7.42 (2 H, m, 2 H of CH aromatic), 7.37 (1 H, t, 1 H of CH, $^{3}J_{HH}$ = 7.6 Hz), 7.09 (1 H, m, 1 H of CH aromatic); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 168.04 ($\underline{C}ONH_2$), 159.59 ($_{Ar}\underline{C}CONH_2$), 136.08 ($\underline{C}OCH_3$), 120.14 ($_{Ar}CH$), 117.56 ($_{Ar}CH$), 113.06 ($_{Ar}CH$), 55.68 ($O\underline{C}H_3$).

4-Nitrobenzamide:



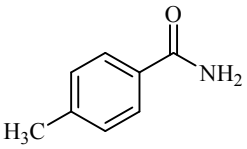
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.34 (1 H, s, 1 H of NH), 8.30 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 8.11 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.8 Hz), 7.75 (1 H, s, 1 H of NH); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 166.70 ($\underline{C}ONH_2$), 149.53 ($_{Ar}\underline{C}NO_2$), 140.39 ($_{Ar}\underline{C}CONH_2$), 129.41 ($_{meta}CH$), 123.93 ($_{ortho}CH$).

4-methoxybenzamide:



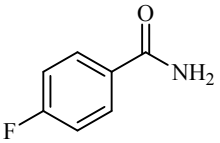
^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.80 (3 H, s, 3 H of OCH_3) 7.86 (2 H, d, 2H of CH aromatic, $^{3}J_{HH}$ = 8.8 Hz), 7.20 (1 H, s, 1 H of NH), 6.98 (2 H, d, , 2 H of CH aromatic, $^{3}J_{HH}$ = 9.2 Hz); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 162.06 ($\underline{C}ONH_2$), 129.84 ($_{ortho}\underline{C}H$), 126.86 ($_{Ar}\underline{C}CONH_2$, $_{Ar}\underline{C}OCH_3$), 113.86 ($_{meta}\underline{C}H$), 55.78 ($O\underline{C}H_3$).

4-methylbenzamide:



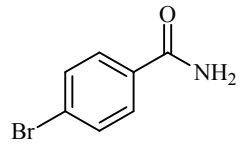
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94 (1 H, s, 1 H of NH), δ 7.78 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 7.28 (1 H, s, 1 H of NH), 7.26 (2 H, d, , 2 H of CH aromatic, $^{3}J_{HH}$ = 8.0 Hz), 2.35(3 H, s, 3 H of CH_3); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 168.25 ($\underline{C}ONH_2$), 141.57 ($_{Ar}\underline{C}CONH_2$), 131.84 ($_{Ar}\underline{C}CH_3$), 129.21 ($_{ortho}$CH), 127.97 ($_{meta}$CH), 21.42 ($\underline{C}H_3$).

4-Fluorobenzamide:



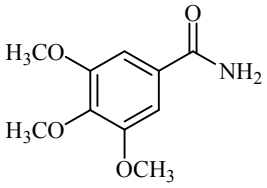
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (1 H s, 1 H of NH), 7.95 (2 H, m, 2 H of CH aromatic), 7.41 (1 H, s, 1 H of NH), 7.28 (2 H, t, 2 H of CH aromatic, $^{3}J_{HH}$ = 9.2 Hz); ^{13}C NMR (100 MHz; DMSO-d_6): d= 167.29 ($\underline{C}ONH_2$), 165.63 ($_{Ar}\underline{C}F$), 163.17 ($_{Ar}\underline{C}CONH_2$), 131.13($_{Ar}$CH), 130.58 ($_{Ar}$CH), 115.58 ($_{Ar}$CH).

4-Bromobenzamide:



^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (1 H, s, 1 H of NH), 7.83 (2 H, d, , 2 H, CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 7.67 (2 H, d, , 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 7.48 (1 H, s, 1 H of NH); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 167.40 ($\underline{C}ONH_2$), 133.80 ($_{Ar}\underline{C}CONH_2$), 131.72 ($_{Ar}CH$), 130.08 ($_{Ar}CH$), 125.52 ($_{Ar}\underline{C}Br$).

3, 4, 5-trimethoxybenzamide:



^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.23 (2 H, s, 2 H of CH aromatic), 3.82 (6 H, s, 6 H of CH aromatic), 3.70 (3 H, s, 3 H of CH aromatic); ^{13}C NMR (100 MHz; DMSO-d_6): δ = 167.76 ($\underline{C}ONH_2$), 140.37 ($_{Ar}\underline{C}CONH_2$), 129.82 ($_{Ar}\underline{C}OCH3$), 105.50 ($_{ortho}CH$), 60.52 ($_{para}CO\underline{C}H_3$), 56.44 ($_{meta}CO\underline{C}H_3$).