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A synthesis and characterization of versatile MgO-ZrO_2 mixed metal oxide nanoparticles and its applications

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Supporting Information-

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General methods and experimental procedure -

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light.

The X-ray powder diffraction pattern was obtained using a conventional powder diffractometer (Philips 1050) using graphite monochromatized Cu-Kα radiation operating in Bragg-Brentano (θ/2θ) geometry. Nitrogen adsorption measurements were carried out at -196°C using Micromeritics ASAP 2020. The BET surface area, S_{BET}, was obtained by applying the BET equation. The total pore volume was evaluated from the amount of nitrogen adsorbed at the highest relative pressure of 0.99. The pore-size distribution was estimated by applying the BJH method to the desorption isotherm. Before each measurement, the samples were degassed at 4 $\times 10^{-3}$ mbar at 200 °C for 10-12 h. The particle size of the catalyst of the catalyst was determined on computerized Inspection system (Galai–Cis–1).

Themogravimetric analysis (TGA) and Diffrential thermal analysis (DTA) under nitrogen atmosphere were carried out by using Seiko instruments Model-326. The thermal traces under air (static) atmosphere were recorded employing mettler Toledo star instruments. The Fourier transform infrared spectrum (FT-IR) of the sample was recorded on a Nicolet–360 FT-IR spectrometer using KBr pellet. The strength of basic sites of MZ catalysts was determined by indicator method.

Transmission Electron Microscopy (TEM) experiments were performed on a Hitachi 8100 microscope with Rontec standard EDS detector and digital image acquisition. The scanning electron microscopy (SEM) analysis (FEI, Quanta 200) was carried out to study the surface morphology. The MgO-ZrO_2 fine powder was placed on carbon stub and the images were recorded at 5-15 kV using LFD detector under low vacuum.

XPS measurements were performed on VSW XPS system with the Class 100 energy analyzer being a part of an experimental setup assembled for surface investigation. The spectra were taken in fixed analyzer transmission mode with the pass energy of 22 eV i.e. FAT 22. The analysis has been performed using the non-monochromatic Al K_α line (photon energy of 1486.3 eV) in order to enable recording the most intensive Mg 1s XPS peak at about 1303 eV. MgO-ZrO_2 fine

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powder was prepared for XPS by pressing on In (Indium) plate as a matrix in order to reduce the charging problems and providing mechanical support. For the energy axis calibration Ag (110) and polycrystalline Au samples (previously cleaned by ion sputtering) were used. The energy was calibrated to the peak position of Ag $3d_{5/2}$ (binding energy of 368.22 eV) and Au $4f_{7/2}$ (binding energy of 83.96 eV) lines.

Preparation of MgO-ZrO_2 –

For the preparation for MgO-ZrO_2, Magnesium nitrate [$Mg(NO_3)_2.6H_2O$] (3.10 g) and zirconium oxychloride [$ZrOCl_2.8H_2O$] (8.11 g) were dissolved together in 2 L flask with 1 L deionized water. Dilute ammonia solution was added dropwise with vigorous stirring (RPM- 5,000) until the precipitation was complete. (Around 6 to 8 h and pH= 10.0) The resultant precipitate was filtered and washed with distilled water till free from chloride ions. The obtained precipitate of metal hydroxide heated in porcelain crucible progressively to 873 K.

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^{1}H NMR and ^{13}C NMR of Compounds

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer at 400 and 100.62, respectively. ^{1}H shifts are reported relative to internal TMS. Carbon shifts are given relative to the ^{13}C signal of $CDCl_3$ (δ 77.0 ppm).

1. (2 E, 6 E)- 2,6-dibenzylidenecyclohexanone[1,2]

3a ; mp 116-118 ^{o}C, Yield 95 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (s, 2H), 7.48–7.26 (m, 10 H), 2.92 (*t*, J=6.0, 4H), 1.81–1.76 (m, 2H) ; ^{13}C NMR ($CDCl_3$) δ: 28.4, 127.5, 128.5, 135.9, 140.9, 144.1, 187.2.

2. (2 E, 6 E)-2,6-bis(4-methoxybenzylidine) cyclohexnone[1, 2]

3b; mp 161-162 ^{o}C, Yield 96 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.76 (s, 2H), 7.45- 6.90 (m, 8H), 3.83 (s, 6H), 2.90 (*t*, J=5.5, 4H), 1.91–1.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ : 28.4, 55.28, 113.8, 127.2, 141.5, 144.3, 159.8, 187.4

3. (2 E, 6 E)-2,6-bis(4-nitrobenzylidine) cyclohexnone[1,2]

3c; mp 163-165 ^{o}C, Yield 94 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.31 (s, 2H), 8.20- 7.59 (m, 8H), 2.96 (*t*, J = 6.0, 4H), 1.91-1.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 27.5, 123.6, 127.1, 141.1, 141.5, 144.3, 147.7, 187.7.

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4. (2*E*, 6 *E*)-2,6-bis((*E*)-3-phenylallylidene)cyclohexanone[1,2]

3 d; mp 176-178 ^{o} C, Yield 97 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.40 (m, 6 H, 3C=H), 7.40- 6.90 (m, 10H), 2.74 (t, J=5.6, 4H), 1.79-1.76 (m, 2H) ; ^{13}C NMR ($CDCl_3$) δ: 27.7, 125.2, 126.0, 127.9, 128.3, 133.8, 142.8, 148.4, 187.3.

5. Benzyl phenylcarbamate[3,7 9]

6a ; Mp 76-77 ^{o}C, Yield 94 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.23 (m, 10 H), 6.94 (b s, 1H), 5.21 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ: 66.8, 118.7, 123.3, 128.1, 128.4, 128.9, 135.9, 137.7, 153.4

6. Benzyl *p*-tolylcarbamate[3,7]

6 b; mp 82 - 83 ^{o}C, Yield 95 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.03 (m, 9 H), 6.70 (b s, 1H), 5.12 (s, 2H), 2.24 (s, 3 H);^{13}C NMR ($CDCl_3$) δ: 20.6, 66.8, 118.8, 128.2, 128.5, 129.4, 132.9, 135.1, 136.1, 153.4.

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7. Benzyl cyclohexylcarbamate[3,8]

6 c ; mp 77-78 ^{o}C, Yield 84 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.25 (m, 5 H), 6.99 (b s, 1H), 5. 08 (s, 2H), 3.99-3.89 (m, 1H), 1.94-1.38 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ: 23.8, 25.5, 33.6, 50.1, 66.6, 128.2, 128.3, 128.5, 128.6, 128.7, 136.9, 155.6.

8. Benzyl mopholine-4-carboxylate[3,9]

6 d; mp 47- 49 °C, Yield 96 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.14 (m, 5H), 5.10 (s, 2H), 3.56-3.41 (m, 4H), 3.49-3.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 44.2, 66.7, 67.3, 127.7, 128.0, 128.6, 136.5, 155.3.

9. Aniline[4,5]

8 a: Yield 94 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.14 (m, 2H), 6.81-6.69 (m, 3 H), 3.57 (b s, 2H); ^{13}C NMR ($CDCl_3$) δ: 115.0, 118.4, 129.2, 146.3.

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10. 4- chloro aniline[4,5]

8 b; Yield 96 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11-7.09 (d, 2H, *J* = 7.48), 6.60 - 6.58 (d, 2H, *J* = 7.52), 3.57 (b s 2H) ; ^{13}C NMR ($CDCl_3$) δ: 116.1, 123.0,129.0, 144.9.

11. 4- methyl aniline[4,5]

8 c; Yield 94 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00 - 6.98 (d, 2H, *J* = 7.12), 6.64 - 6.62 (d, 2H, *J* = 7.08), 3.44 (b s, 2H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 20.3, 115.1, 127.6, 129.6, 143.7.

12. 4-methoxy aniline[4,5]

8 d; Yield 90 %,^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.75-6.73 (d, 2H, *J*= 7.2), 6.65 - 6.63 (d, 2H, *J* = 7.6), 3.74 (s, 3H), 3.15 (b s, 2H); ^{13}C NMR ($CDCl_3$) δ: 55.7, 114.8, 116.4, 139.9, 152.8.

13. 2,2,4-trimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine[6]

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9 a; mp 135-136 ^{o}C, Yield 97 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33- 6.57 (m, 4H), 2.99 (b s, 1H, NH), 2.37 (s, 3H), 2.24 (s, 2H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$) δ: 29.8, 30.6, 45.1, 68.4, 121.6, 122.2, 125.7, 126.9, 137.8, 140.7, 172.9.

14. 2,3,9,10a-tetrahydro-1*H*-spiro[benzo[*b*]cyclopenta[e][1,4]diazepine-10,1'-cyclopentane][6]

9 b; mp 137-138 ^{o}C,Yield 95 % ; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76- 6.53 (m, 4H), 3.90 (b s, 1H, NH), 2.50-1.20 (m, 15H); ^{13}C NMR ($CDCl_3$) δ: 23.1, 24.4, 24.6, 28.7, 33.7, 38.4, 39.3, 54.3, 67.4, 118.9, 119.3, 126.9, 132.4, 139.6, 143.6, 178.6.

15. 1',2',3',4'10'11a'-hexahydrospiro[cyclohexane-1,11'-dibenzo[b,e][1,4]diazepine][6]

9 c; mp 136-137 ^{o}C,Yield 92 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63- 6.85 (m, 4H), 3.49 (b s, 1H, NH), 2.38- 0.90 (m, 19H); ^{13}C NMR ($CDCl_3$) δ: 21.6, 21.9, 23.4, 23.5, 24.7, 25.3, 33.4, 34.6, 39.5, 40.8, 52.5, 63.4, 121.7, 126.6, 129.8, 138.3, 142.5, 178.6.

16. 2-methyl-2-4-diphenyl-2,3-dihydro-1-*H*-benzo[*b*][1,4]diazepine[6]

9 d; mp 150-151 ^{o}C, Yield 93 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.67- 7.58 (m, 2H), 7.49 - 7.31 (m, 10 H), 7.11 - 6.64 (m, 2H), 3.38 (b s, 1H, NH), 3.16 (d, J= 12.8, 1H), 2.92 (d, J= 12.8, 1H),

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1.73 (s, 3H) ;^{13}C NMR ($CDCl_3$) δ: 29.5, 41.3, 74.2, 121.5, 122.1, 125.6, 126.9, 127.4, 127.5, 128.4, 128.6, 128.8, 129.9, 138.2, 139.4, 140.7, 145.5, 166.5.

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