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A Synergistic Effect of Cobalt Schiff Base Complex and TiO_2 Nanoparticles on Aerobic Olefin Epoxidation

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Experimental

General remarks

All chemicals were purchased from Merck or Fluka. FTIR spectra were recorded on a NICOLET spectrometer. Thermogravimetric analysis (TGA) of powders was performed in air by Shimadzu 50. TEM images were obtained with a 906 E instrument (Zeiss, Jena, Germany). Samples for TEM experiment were prepared by dispersion in ethanol, sonicating for 30 min, and evaporating one drop of the solution onto a 200 mesh *formbar-coated copper grid.* XP spectra were recorded using a BESTEC GMBH (10^{-10} mw) with Al anode. Diffuse reflectance UV–Vis spectra were recorded using an Avantes spectrometer (Avaspec-2048-TEC model). Progress of each reactions was monitored by TLC using silica-gel SIL G/UV 254 plates and also by GC on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column. NMR spectra were recorded on Bruker Avance DPX 250 and 400 MHz instruments.

- The Preparation of organosilicon aldehyde

To a solution of (3-Chloropropyl) trimethoxysilan (0.74 mL, 4 mmol) in DMSO (0.35 mL, 5 mmol) was added $NaHCO_3$ (0.67 g, 8 mmol). The solution was refluxed at 155 ºC for 2 h. Then, water (50 mL) was added to the reaction mixture and the product extracted with Et_2O (2 × 50 mL). The organic layer was separated and dried over anhydrous $CaCl_2$ and filtered. Evaporation of the solvent afforded the desired product (yellow oil, 70 % Isolated yield). Structural assignments of the product is based on their FT-IR, ^1H NMR [21].

- The Preparation of Schiff base ligand

To a solution of (3-oxopropyl) trimethoxysilan (0.8 mL, 5 mmol) in ethanol (10 mL) was gradually added a solution of ethanol amine (0.3 mL, 5 mmol) in ethanol (10 mL) at 60 ºC under ultrasonic agitation. Then, the reaction mixture remained under the same conditions for 60 min. Afterwards, the product which was precipitated after 24 hoursat room temperature, filtered and washed with ethanol and dried in desiccators. (85 % isolated yield) Structural assignments of the product is based on their FTIR, ^{1}H NMR [21].

- The Preparation of Co(II)Schiff base complex

A solution of cobalt acetate (0.44 g, 2.5 mmol) in ethanol (10 mL) was added to a solution of shiff base ligand (5 mmol, 0.25 g) in 10 ml ethanol at 60 ºC under ultrasonic agitation. Then, the reaction mixture remained under the same conditions for 3 hours. The complex which was precipitated after cooling the reactionmixture, filtered and washed with cold ethanol. Finally, Co(II)Schiff base complex was obtained after drying at 100 °C under vacuum. (92 % isolated yield). Structural assignments of the product is based on their FTIR, ^{1}H NMR [21].

- Fabrication of TiO_2 nanoparticles

To a solution of $TiCl_3$ (0.05 mol) in a mixture of double-distilled water and absolute ethanol (1:1) was added citric acid (0.15 mol) and ethylene glycol (0.15 mol) subsequently. The resulting mixture was dissolved at 45 ºC under ultrasound for 15 min to give a clear violet solution. The solution was refluxed at 120 ºC for 8 h which turned into a metal-citrate homogeneous complex with a little color change from clear violet to black-violet. After cooling down, in order to bring about the required chemical reactions for the development of polymerization and evaporation of the solvent, the sol was further slowly heated at 90 ºC for 6 h in an open bath until a beige wet gel was obtained. During continuous heating at this temperature, the polymerization between citric acid, ethylene glycol and complexes is developed and ultimately sol became more viscous as a wet gel. In the final step of sol-gel process, the wet gel was fully dried by direct heating on the hot plate at 150 ºC for 6 h. The resultant production was a black powder. Then it was calcined in a furnace at 600 ºC for 3 h at a rate of 5 ºC/min. Finally TiO_2 nanoparticles with a white color were obtained [22].

- Preparation of TiO_2/CoL_2 nanocomposite

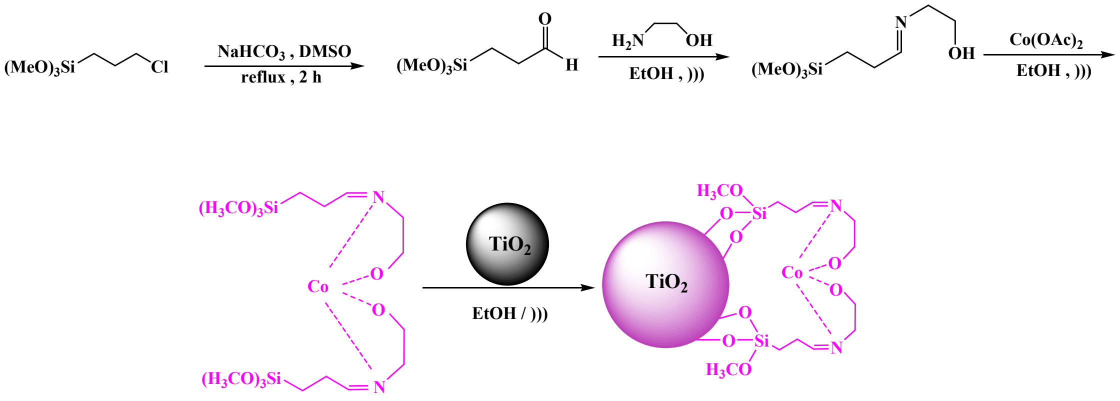
To 1.0 g of TiO_2 nanoparticles was gradually added 1.0 g CoL_2 in ethanol over a period of60 minat 60 °C underultrasonic agitation. Then, the as-obtained mixture was refluxed for 6 h.Afterwards, the product was centrifuged and washed by ethanol. Finally, CoL_2@TiO_2 nanocomposite was obtained after drying for 3h at 70 °C (scheme S1).

- General procedure for aerobic oxidation of olefines

To a mixture of olefin (1 mmol) and CoL_2@TiO_2nanohybrid (0.75mol %) in acetonitril (2 mL) was added NHPI (5mol %) and the reaction mixture was stirred under 1 atm. O_2 (7−10 mL/min) and visible light at 65 ºC for the required time. The reaction progress was monitored by GC, and the yields of the products were determined by GC and NMR analysis.

Reusability of catalyst

To a mixture of norbornene (1 mmol) and $CoL_2@TiO_2$nanohybrid (0.75mol %) in acetonitril (2 mL) was added NHPI (5mol %) and the reaction mixture was stirred under 1 atm. O_2 (7−10 mL/min) and visible light at 65ºC for 5 h. After completion of the reaction, $CoL_2@TiO_2$nanohybridwas separated by centrifuging followed by decantation (3×5 mL ethylacetate). The isolated solid phase $CoL_2@TiO_2$nanohybrid) was washed with ethanol then dried under reduced pressure and reused for next runs.



Scheme S1. Preparation of $CoL_2@TiO_2$nanocomposite

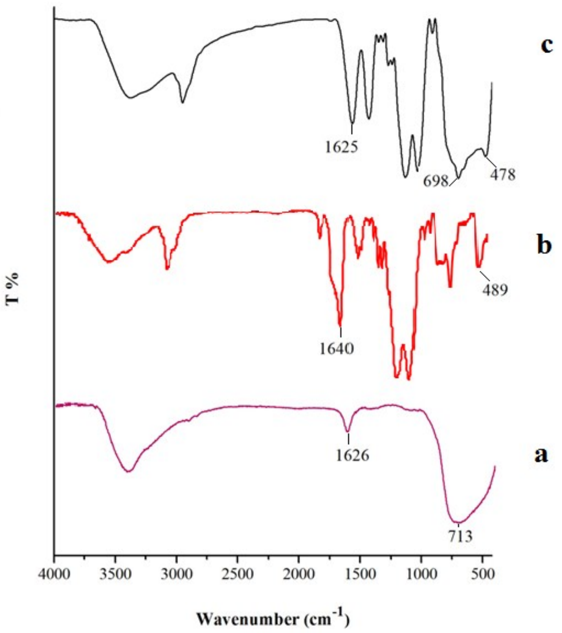


Fig. S1. FT-IR spectra of (a)TiO_2 nanoparticles, (b) Co(II)Schiff base complexand (c)$CoL_2@TiO_2$

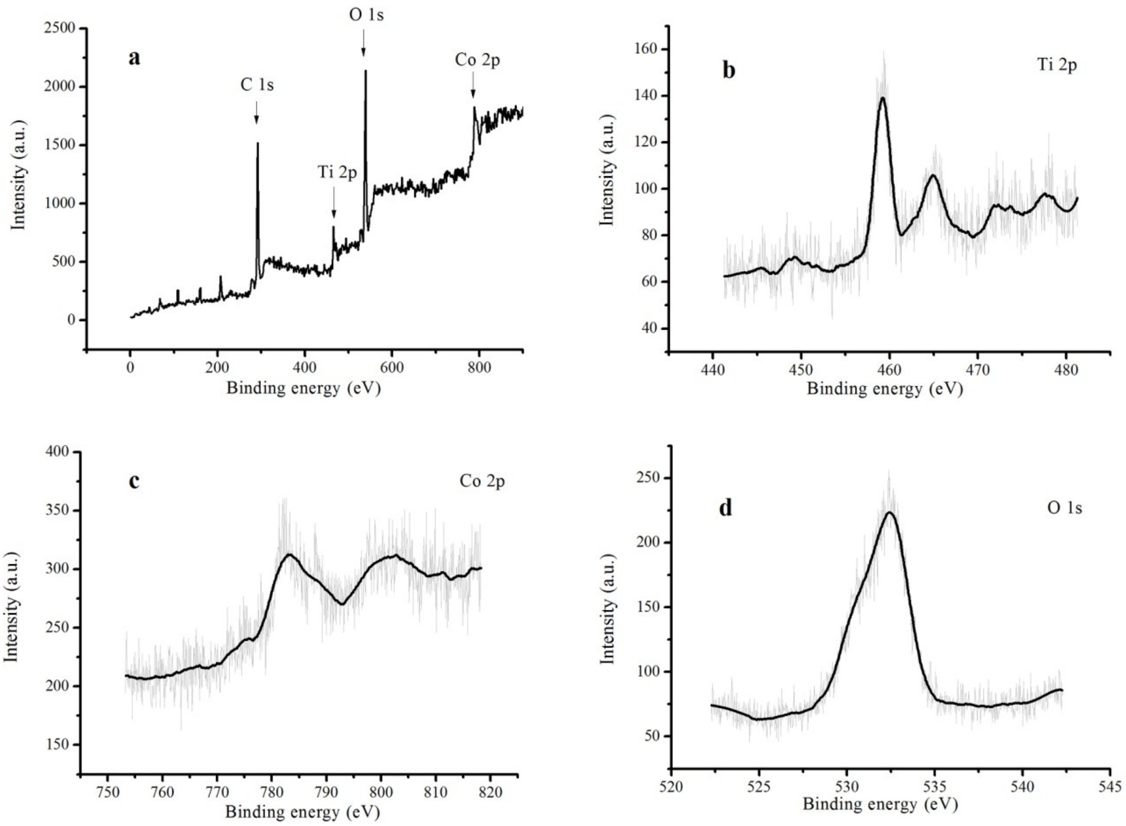


Fig.S2. XPS spectra of $CoL_2@TiO_2$nanocomposite (a) wide scan, (b) Ti 2p, (c) Co 2p, and (d) O 1s.

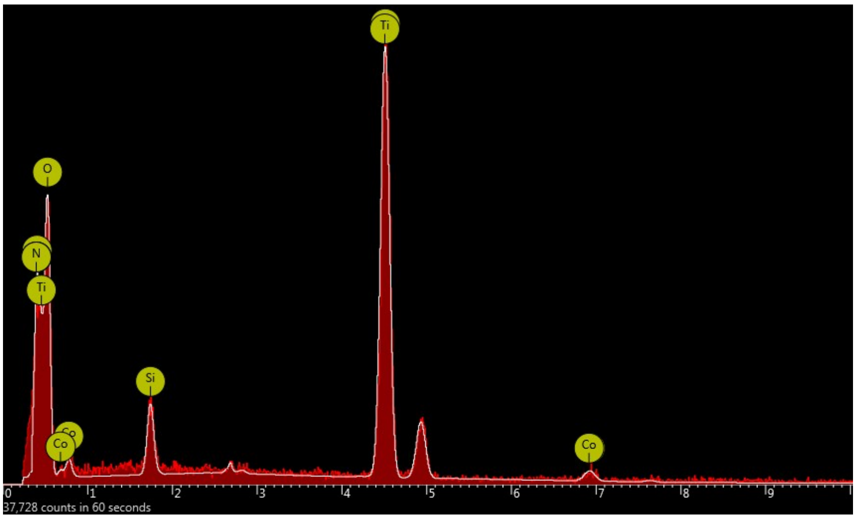


Fig.S3. EDX analysis of TiO_2/CoL_2nanocomposite

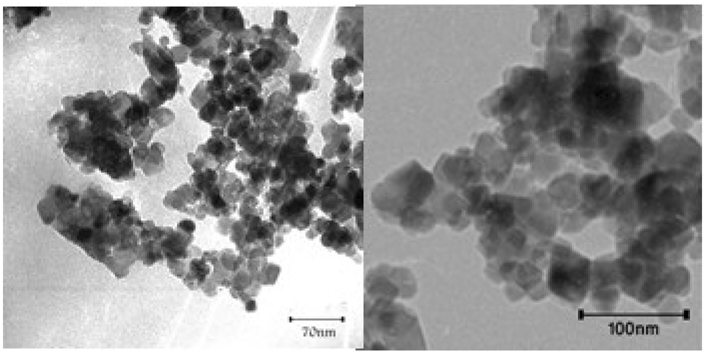


Fig. S4.TEM images of TiO_2 (left) and $CoL_2@TiO_2$nanocomposite(right)

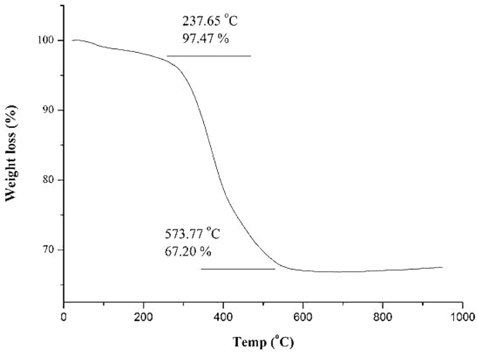


Fig. S5.The TGA of $CoL_2@TiO_2$nanocomposite

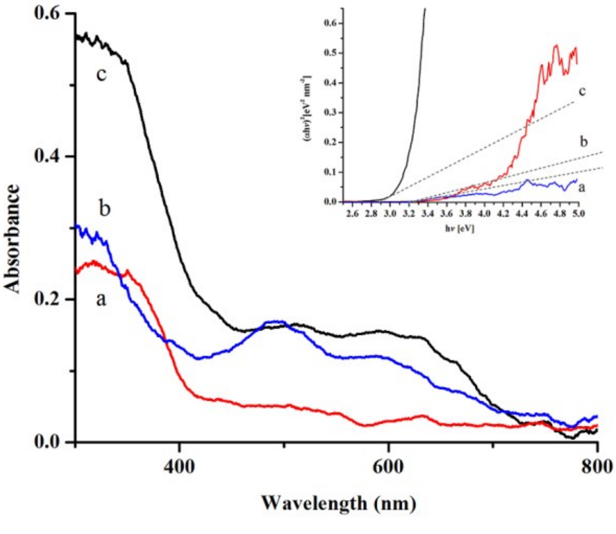


Fig.S6. Diffuse reflectance UV–vis spectra of (a) bare TiO_2 NPs, (b) $CoL_2$and (c) $CoL_2@TiO_2$