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Functionalized montmorillonite supported rhodium complexes: Efficient catalysts for carbonylation of methanol

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ABSTRACT

The catalyst precursors, [Rh(CO)$_2$Cl-ligand(L)-APTMS-montmorillonite] (**1a** and **1b**, where, **a** and **b** correspond to ligand (L)-APTMS-montmorillonite for ligands L = Quinoline-2-carboxylic acid (L$_1$) and Quinoline-8-carboxylic acid (L$_2$) respectively; APTMS = (3-aminopropyl)-trimethoxysilane), have been synthesised. The montmorillonite was activated by treating with formic acid under controlled condition to increase the surface area and pore volume prior to functionalization by APTMS and subsequent anchoring with the ligands. **1a** and **1b** were characterized by CHN, FT-IR, powder XRD, N$_2$-sorption and SEM-EDX analysis. The efficacy of the catalysts was evaluated in carbonylation of methanol to acetic acid and found to exhibit catalytic conversion up to 99.9%. The catalysts were recovered and reused for several runs without any significant loss of catalytic efficiency.

1. Introduction

Acetic acid is one of the vital chemical used in laboratory as well as for industrial process [1–3]. It is used in very large scale in industries like textile, food processing, ink & printing adhesive etc. The most common way for industrial production of acetic acid is the catalytic carbonylation of methanol by Monsanto's process. The active species in Monsanto's process is $[Rh(CO)_2I_2]^-$ which works together with co-catalyst CH_3I [4–7]. Considerable efforts are being made in order to improve the catalyst in various ways by incorporating different ligands into the coordination sphere of the catalyst [8–14]. Among these, ligands containing P, N or N∼O atoms are more widely studied because of their σ-bonding and π-back bonding capacity (for P atom) through which they can stabilize low valent metals. Furthermore because of their good σ-donating ability, they make the metal center more electron rich. As a result, the metal center becomes more susceptible to oxidative addition, which is the primary step of carbonylation reaction [1,2,14–30].

However, all these catalytic processes are homogeneous in nature and always associated with problems of catalyst separation and reusability, which is very important from the point of economic viability. This problem can be overcome by using heterogeneous catalyst or by immobilizing homogeneous catalyst on heterogeneous support for easy separation. A large number of studies have already been reported on the anchoring of such metal complexes onto the solid inorganic supports (e.g., silica, mesoporous materials, zeolites), polymers etc. [31–37]. Apart from immobilized Rh-catalyst for the carbonylation of methanol to acetic acid, studies using other metals like Ni, Ir etc. are also reported [36–39,41]. Herein, we have reported the synthesis of two anchored Rh complexes (**1a** and **1b**) prepared through complexation of $[Rh(CO)_2Cl]_2$ with two different quinoline carboxylic acids immobilized on APTMS functionalized activated montmorillonite clay (F-mont.). As a part of our continuing research activity [8,9,14,17,18,25–28,42], two N∼O donor ligand, quinoline-2-carboxylic acid (**L**$_1$) and quinoline-8-carboxylic acid (**L**$_2$) are taken for carrying out the carbonylation of methanol. **L**$_1$ is immobilized on F-mont. resulting **a** and subsequent anchoring of $[Rh(CO)_2Cl]_2$ gives **1a**. Similarly, immobilization of **L**$_2$ on F-mont. results **b** and subsequent anchoring of $[Rh(CO)_2Cl]_2$ gives **1b**. The anchored Rh complexes were evaluated as a catalyst precursor for the carbonylation of methanol to acetic acid with up to 99.9% conversion and only acetic acid was

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obtained as a single product without yielding methyl acetate as side product. Moreover, the catalyst precursors were very stable and can be easily separated from the reaction mixture by simple filtration. The catalysts were found very active for several runs without any significant loss of activity.

2. Experimental

2.1. Materials and methods

Bentonite (procured from Gujarat, India), containing quartz, iron oxide etc. as impurities, was purified by sedimentation technique to collect the montmorillonite clay (mont.) of <2 μm fraction before use. PXRD analysis of the air dried purified fraction shows the basal spacing (d_{001}) to be about 12.5 Å, which indicates that the purified fraction is mont. The surface area of the pure mont., determined by N_2-sorption, was found about 101 $m^2 g^{-1}$. The analytical oxide composition of the bentonite determined was SiO_2: 49.42%; Al_2O_3: 20.02%; Fe_2O_3: 7.49%; MgO: 2.82%; CaO: 0.69%; loss on ignition (LOI): 17.51%; and others (Na_2O, K_2O and TiO_2): 2.05%. All solvents were distilled under nitrogen environment prior to use. $RhCl_3{\cdot}3H_2O$ (Rh content 40%) was purchased from M/S Arrora Matthey Ltd., Kolkata, India. Quinoline-2-carboxylic acid and Quinoline-8-carboxylic acid ligands (98%) were purchased from M/S Aldrich, USA and used without further purification. Formic acid (98–99%), dichloromethane (99%), acetone (99%), toluene (99.5%), acetonitrile (99.5%), acetone and methanol (99.5%) were purchased from Sisco Research Laboratories Pvt., Ltd. (India) and used after distilled using standard techniques. Methyl iodide (99.5%), KBr (IR grade) and $CHCl_3$ (IR grade) were purchased from M/S Merck, Germany and used without further purification. Carbon monoxide gas (99.9%) was purchased from Alchemie gases and chemicals Pvt., Ltd. (India).

Elemental analyses were performed on a PerkinElmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs and $CHCl_3$ on a Shimadzu IR Affinity-1 spectrophotometer. The carbonylation reactions of methanol were carried out in a high pressure reactor (Parr-4592, USA) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). Powder XRD spectra were recorded on a Rigaku, Ultima IV X-ray diffractometer for 2θ from 2° to 80° using Cu-Kα source ($\lambda = 1.54$ Å). Surface area, pore volume and average pore diameter were measured by N_2 adsorption analysis using Autosorb-1 surface area analyser (Quantachrome USA). Surface areas of the samples were calculated applying the Branauer–Emmett–Teller (BET) model. Prior to adsorption, the samples were degassed at 250 °C for 3 h. Pore size distributions were derived from desorption isotherms using Barrett–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) were obtained with Leo 1430 vp operated at 3 and 10 kV. Prior to examination, the samples were coated with gold.

2.2. Support preparation

10 g of powdered mont. was dispersed in 500 mL of 10 M formic acid solution and refluxed for 16 h. The whole mass was transferred to a beaker and the solvent was decanted off. The remaining mass was mixed with distilled water and centrifuged. Finally, the centrifuged mass was dialysed with distilled water till the conductance of the dialysed water becomes equal to that of pure distilled water. The whole mass was recovered and dried at 65 °C. The sample thus prepared was designated as AT-mont.

Analytical data for the prepared support are as follows: Yield: 9.945 g, BET surface area: 257 $m^2 g^{-1}$, average pore diameter: 47 Å, pore volume: 0.30 $cm^3 g^{-1}$, XRD data: $2\theta = 7.06°$, 26°.

2.3. Preparation of Rhodium dimer $[Rh(CO)_2Cl]_2$

$[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3{\cdot}3H_2O$ at 100–110 °C in the presence of moisture [29]. The red crystals were collected in a sample tube and kept in desiccators under vacuum.

2.4. Synthesis of APTMS functionalized AT-mont.

500 mg of AT-mont.was added to 100 mL of dry toluene. To this mixture 0.5 mmol of APTMS was added and the resultant mixture was refluxed for 6 h. After cooling, the solid was separated by filtration and washed repeatedly using soxhlet extraction with dry toluene as a solvent. The resultant material was dried and designated as F-mont.

Analytical data for F-mont.: Yield: 490 mg, FT-IR data (KBr) (cm^{-1}): 1638, 2931, 3299, ^{29}Si NMR (79.5 MHz) δ(ppm): −93 and −110, CHN analysis data: C (10.86%), H (2.49%) and N (2.89%).

2.5. Synthesis of $\mathbf{L}_1$ and $\mathbf{L}_2$ immobilized F-mont

In a suspension of 400 mg F-mont.in 60 mL acetone, 0.17 mmol of $\mathbf{L}_1$ was added. The reaction mixture was refluxed for 4 h. The solids were separated from the solvent by filtration and washed repeatedly using soxhlet extraction with DCM. The solid mass was air dried and kept in desiccators. The material was designated as **a**. The same process was repeated with ligand $\mathbf{L}_2$ and the material thus prepared was designated as **b**.

Analytical data for **a**: Yield: 387 mg, FT-IR data (KBr) (cm^{-1}): 3444, 3419, 3367, 2940, 1707, 1635, 1465, 1381, CHN analysis data: C (12.56%), H (2.66%) and N (3.09%).

Analytical data for **b**: Yield: 388 mg, FT-IR data (KBr) (cm^{-1}): 3443, 3430, 3311, 2939, 1708, 1634, 1471, 1384, CHN analysis data: C (12.69%), H (2.71%) and N (3.07%).

2.6. Immobilization of Rh complexes on **a** and **b**

Anchoring of Rh complexes on **a** and **b** was done through complexation of $[Rh(CO)_2Cl]_2$ with the anchored ligand $\mathbf{L}_1$ and $\mathbf{L}_2$ on F-mont. 96.5 mg of the dimer was added to a suspension of **a** (400 mg) in acetonitrile and stirred for 30 min under CO environment. The solid was then filtered and washed on the filter paper with acetonitrile to remove any un-anchored rhodium dimer. The mass was air dried, kept in desiccator and designated as **1a**.The same procedure was followed using the material **b** and the material was designated as **1b**.

Analytical data for **1a**:Yield: 390 mg, FT-IR data (KBr) (cm^{-1}): 3444, 3419, 3367, 2940, 2087, 2011, 1635, 1377, BET surface area: 87 $m^2 g^{-1}$, pore diameter: 31 Å, Pore volume: 0.24 $cm^3 g^{-1}$, XRD data: $2\theta = 7.06°$, 27°, ^{29}Si NMR (79.5 MHz) δ(ppm): −55, −65, −92, −107, ^{13}C NMR (100.6 MHz) δ(ppm): 21, 71, 124, CHN analysis data: C (12.93%), H (2.61%) and N (3.02%).

Analytical data for **1b**: Yield: 390 mg, FT-IR data (KBr) (cm^{-1}): 3443, 3430, 3311, 2939, 2082, 2010, 1634, 1471, 1370, BET surface area: 75 $m^2 g^{-1}$, pore diameter: 55 Å, Pore volume: 0.13 $cm^3 g^{-1}$, XRD data: $2\theta = 7.06°$, 27°, ^{29}Si NMR (79.5 MHz) δ(ppm): −47, −55, −65, −92, −107, ^{13}C NMR (100.6 MHz) δ(ppm): 25, CHN analysis data: C (12.98%), H (2.69%) and N (3.11%).

2.7. Catalytic carbonylation reaction

40 mg of the catalyst (**1a** or **1b**) with 1 mL of CH_3I was taken in the reaction vessel and kept for 1 min. To it 4 mL of CH_3OH and 1 mL of distilled water was added. Then the reactor was pressurized with CO gas to 10, 15 or 20 bar at room temperature (r.t.). The reaction was carried out for 1 h and 3 h at 130 ± 2 °C with corresponding CO