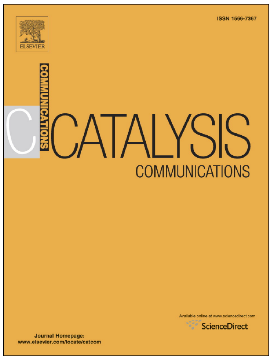

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The Co-MOF-74 Modified With N,N'-Dihydroxypyromellitimide For Selective, Solvent Free Aerobic Oxidation of Toluene.

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Abstract

The present research reports on a successful strategy for the modification of a cobalt-containing metal-organic framework (Co-MOF-74 aka Co-CPO-27) with NDHPI for enhanced catalytic activity in the aerobic oxidation of alkyl-benzenes under mild reaction conditions. We present here the synthesis and characterization of the Co-MOF-74@NDHPI composite. The experimental results show the successful incorporation of NDHPI molecules into the Co-MOF-74 metal-organic framework. The application of the Co-MOF-74@NDHPI composite in the heterogeneous solvent-free oxidation of toluene with molecular oxygen as primary oxidant showed a high catalytic performance with 16% conversion and more than 30% selectivity towards benzoic acid in 2 hours at 100 ºC, O_2: 1.6 MPa.

1. Introduction

Catalysts have been widely applied in the main technologies for the development of the world economy. Among which, the selective oxidation of carbon-hydrogen bonds using dioxygen as a "green" oxidant is of crucial importance in allowing the sustainable activation of raw materials to form valuable chemicals and intermediates in many important industrial processes, one of which is the selective oxidation of hydrocarbons to corresponding oxygenated products[1]. Oxygen is the most abundant and available oxidizing agent. Although it is of high commercial interest its direct utilization for industrial applications is highly limited due to the high activation energy and as a result harsh reaction conditions[2], thus catalysts are typically required. N-hydroxyphthalimide (NHPI) has been introduced as an effective catalyst for C-H oxidation[3]. NHPI acts as a precursor of phthalimido-N-oxyl (PINO) radical, which is the effective abstracting species in all of the free radical processes. During the past few decades a combination of NHPI and cobalt salts was reported to be a valuable catalytic system for aerobic oxidation and functionalization of a large number of organic substrates [5,6].

One of the straightforward approaches in the catalytic oxidation processes is the impregnation of N-hydroxyphthalimide (NHPI), a cheap and nontoxic organocatalyst, in the pores of metal-organic framework materials [7] which simultaneously combine properties that are highly desirable for the design of heterogeneous catalysts: a large surface area, high porosity and high metal content. Such composite materials show superior performance in selective oxidations of different organic compounds [8–15] Although, the research is focusing mostly on modification of Cu and Fe MOFs with NHPI, it has been postulated in homogeneous catalysis that cobalt is the most effective initiator of PINO radical formation [4], moreover the multi-nitroxy organocatalysts such as N,N'-Dihydroxypyromellitimide (NDHPI) showed enhanced catalytic oxidation efficiencies in most cases, even if smaller amounts of catalysts are used[16]. On this basis, Co-MOF-74 was chosen as a carrier and co-catalyst for the NDHPI molecule. It provides 1.1-1.2 nm large pores [17] enabling appropriate mass transfer and thus it is suitable for modification with large molecules. Herein, we report the preparation and characterization of Co-MOF-74@NDHPI composite, which can be used as an effective heterogeneous catalyst in the solvent-free oxidation of toluene.

2. Experimental

2.1. Materials

All the reagents and solvents used were commercially supplied (Sigma, Aldrich, Alfa Aesar). The GC standard used and the methanol were of high purity.

2.2. Synthesis of Co-MOF-74

Co-MOF-74 was synthesized using the conventional solvothermal method following a procedure reported in the literature [18]: a solid mixture of H_4DHBDC (2,5-dihydroxy benzenedicarboxylic acid, 0.729 mmol) and $Co(NO_3)_2{\cdot}6H_2O$ (cobalt nitrate hexahydrate, 2.45 mmol) was added to a 1:1:1 mixture of DMF-ethanol-water (60 mL) in a 100 mL Duran bottle, and stirred for 1 h until it became homogeneous. The reaction vial was capped tightly and placed in an oven at 100 ºC. After 24 h, the bottle was removed from the oven and allowed to cool to room temperature. The MOF crystals were separated by filtration and soaked in methanol for 24 hours under stirring, in order to exchange the DMF that remained in the pores of the material. Methanol was replaced three times during the procedure.

2.3. Preparation of Co-MOF-74@NDHPI

First, a synthesis of NDHPI was performed according to a procedure reported in the literature [19]: Hydroxylamine hydrochloride (38.4 mmol) and trimethylamine (Et_3N) (38 mmol) were dissolved in 120 mL of absolute ethanol. After stirring for 10 min, a 1,2,4,5-benzenetetracarboxylic anhydride (19.6 mmol) was added to the solution, which was then refluxed for 8 h. The resulting red solution was poured into ca. 200 mL of H_2O. The product precipitated as a yellow powder, which was filtered and vacuum-dried at 50 ºC.

In the second step, 0.2 g (0.8 mmol) of NDHPI was dissolved in 10 mL of methanol : acetonitrile mixture (1:1). To this solution, 1 g (3.2 mmol) of Co-MOF-74 was added. Prior the addition, Co-MOF-74 was activated at 200°C for 5h under a vacuum. The resulting suspension was heated at 50 ºC overnight. After that, the mixture was cooled and the solvent was evaporated. The resulting material was then dried at 80 ºC.

2.4. Catalyst characterization

Powder X-Ray diffraction (XRD) was performed on a PANalytical X´Pert PRO diffractometer with Cu Kα radiation (λ=1.5406 Å). in the 2θ range from 5º to 50º (100 s per step of 0.034º) using a fully opened X'Celerator detector.

Thermogravimetric analysis (TGA) was performed using a Q5000IR (TA Instruments, Inc.) device under air flow (25 mL min^{-1}) from 25 to 700 ºC, with a heating rate of 10 ºC min^{-1}.

The IR spectra of the samples dispersed in KBr pellets were recorded using a PerkinElmer FTIR Spectrum 100 spectrometer with a 4 cm^{-1} resolution in the frequency range of 4000–400 cm^{-1}.

A Zeiss SUPRA 35 VP scanning electron microscope (SEM) was used for microstructural analysis.

2.5. Adsorption measurements

Nitrogen adsorption was performed using a Micromeritics Tristar 3000 automated gas adsorption analyzer at −196 °C before the measurement samples were degassed in vacuum at 200 ºC for 5h. The specific surface area of the solid samples was calculated using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range of P/P^0 = 0.05–0.25. The total pore volumes were determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.95.

Toluene and benzene sorption analysis was performed using an IGA-100 gravimetric analyzer (Hiden Isochema Ltd.). Toluene sorption isotherms were measured at 25 °C in a relative pressure range from 0 to 0.9. Prior to the measurements, the samples were degassed at 200 °C in a vacuum.

2.6. Typical procedure of toluene oxidation

Toluene (5 g) and the pre-prepared catalyst (0.4 g) were placed into a 100 mL Parr mini benchtop reactor (model 4565). The reactions were carried out at 100 ºC in an oxygen atmosphere (1.6 MPa) for 2 hours. After that, the catalyst was filtered and washed with chloroform. The reaction mixture was analysed using a Varian 3900 gas chromatograph equipped with a Varian CP-Porabound U column with a diameter of 0.32 mm and a length of 25 m. Quantification was performed by using chlorobenzene as the GC standard. A given amount of chlorobenzene was added to a known aliquot of the sample and the solution was injected into the GC machine to determine the percentage selectivity and the percentage conversion.

3. Results and discussion

3.1. Catalyst characterization

The Co-MOF-74@NDHPI composite was obtained via the wet impregnation technique and along with the starting Co-MOF-74 material, it was characterized by XRD, FT-IR and TGA, Figures 1, 2, and 3 respectively.

The XRD patterns of Co-MOF-74 and Co-MOF-74@NDHPI are very similar and are in good agreement with the pattern reported for Co-MOF-74 elsewhere in the literature [20,21]. Both samples show good crystallinity with strong characteristic peaks at 2 theta: 6.8; 11.9; 16.8; 18.1; 21.6 degree, representing a single phase of Co-MOF-74. It is clear that the impregnation of NDHPI into Co-MOF-74 did not change the crystal structure.

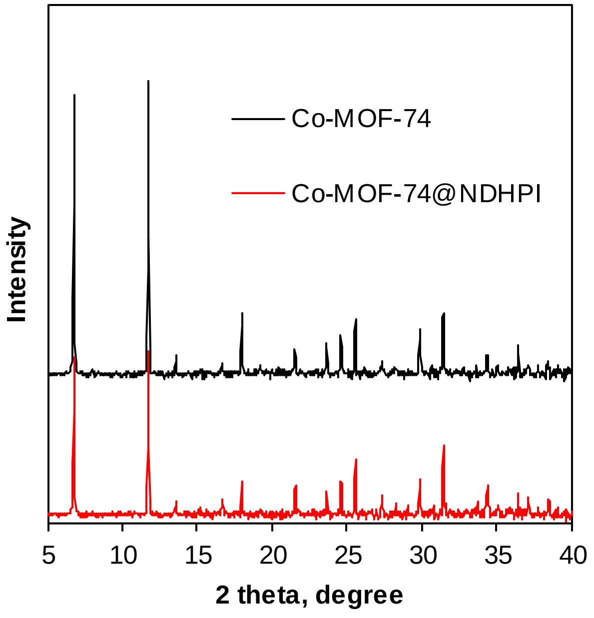

Figure 1. XRD patterns of the Co-MOF-74 and Co-MOF-74@NDHPI samples.

The FTIR spectra of the Co-MOF-74 and Co-MOF-74@NDHPI samples shows typical bands of carboxyl groups located at 1650-1550 cm^{-1} and 1400-1350 cm^{-1} corresponding to asymmetric and symmetric stretching, respectively. The broad band with the maximum at 3280 is related to OH groups of coordinated water molecules. The absence of the characteristic peak at around 2970 cm^{-1} indicates that the DMF solvent was effectively removed. The appearance of the new peaks with maximums at 1780, 1710, 900, 700 and 550 cm^{-1} at Co-MOF-74@NDHPI spectrum indicates that the NDHPI was successfully impregnated.

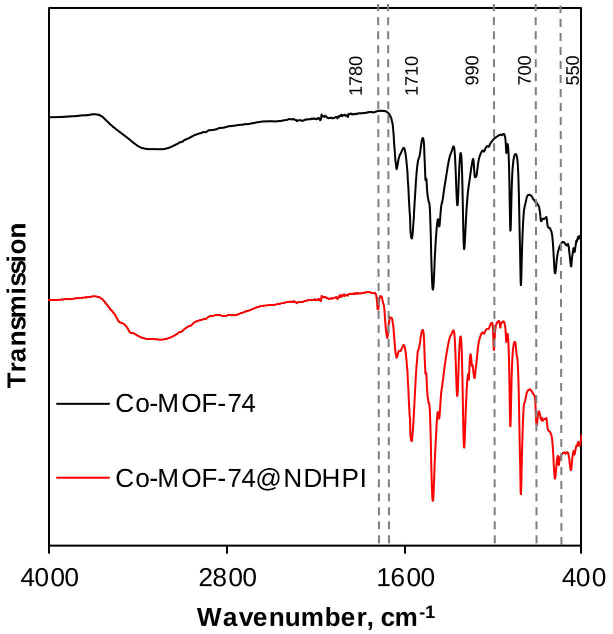

Figure 2. FTIR spectra of the Co-MOF-74 and Co-MOF-74@NDHPI samples.

Figure 3 compares the thermogravimetric profiles of the Co-MOF-74 and Co-MOF-74@NDHPI samples. The thermogram of the Co-MOF-74 sample shows two regions matching those published elsewhere[22] for Co-MOF-74 material in terms of the magnitude of the weight loss and the order of thermal stability. The first weight loss (22 %) region between 30 and 150 ºC indicates the loss of moisture and perfectly coincides with the first weight loss of the Co-MOF-74@NDHPI sample. The second weight loss region starts at 250 ºC, where the structure of Co-MOF-74 collapses and the organic linker is burned. The maximum temperature of the linker decomposition at Co-MOF-74 is in good agreement with the literature [22]. Modification with NDHPI slightly increases the maximum temperature of the ligand decomposition from 290 ºC in Co-MOF-74 to 315 ºC due to the higher maximum temperature of the NDHPI decomposition (320 ºC) Fig.S1 (supporting information). The TGA results indicate that the impregnated amount of NDHPI in the modified Co-MOF-74 is ~5%, which is in agreement with the calculated loading.

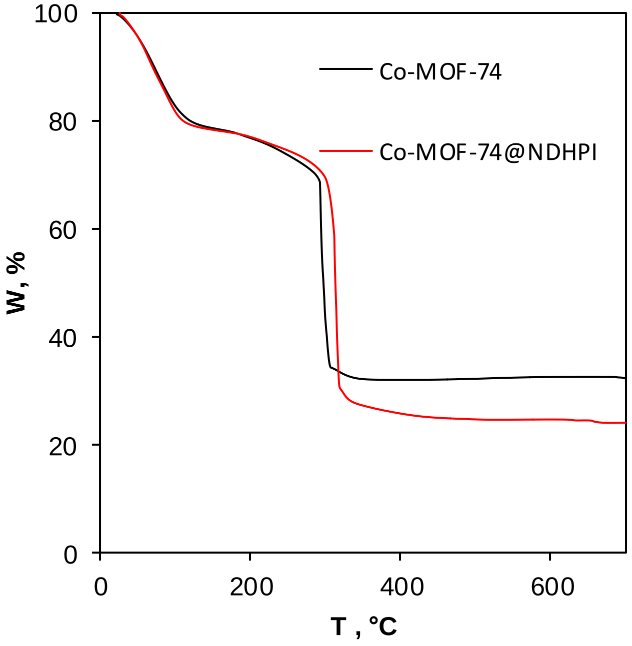

Figure3. TGA curves of the Co-MOF-74 and Co-MOF-74@NDHPI samples.

The toluene adsorption isotherms (Figure 5) show a 10 wt.% decrease in the total uptake of toluene on Co-MOF-74 sample after modification with NDHPI, from 34 wt.% for Co-MOF-74 to 24 wt% for Co-MOF-74@NDHPI. Further, the adsorption of benzene, which has similar properties to toluene and is one of the common sorbates used for determining the specific surface area, was applied to determine the BET surface area and the total volume of the pores of the samples. The obtained results are listed in Table 1. It can be seen that after the incorporation of NDHPI, the surface area and total volume of the pores in Co-MOF-74@NDHPI sample decreased sharply in comparison with unmodified Co-MOF-74. Moreover, the results on pore size distribution Fig. S2 (supporting information) indicate decrease in the relative pore filling for composite material in the range of average pore diameter 10 – 20 Å. These findings were further supported by the N_2 sorption measurements (Table 1). The results show the same trend in the decrease of surface characteristics of the samples and provide significant evidence of the internal location of the NDHPI in composite material.

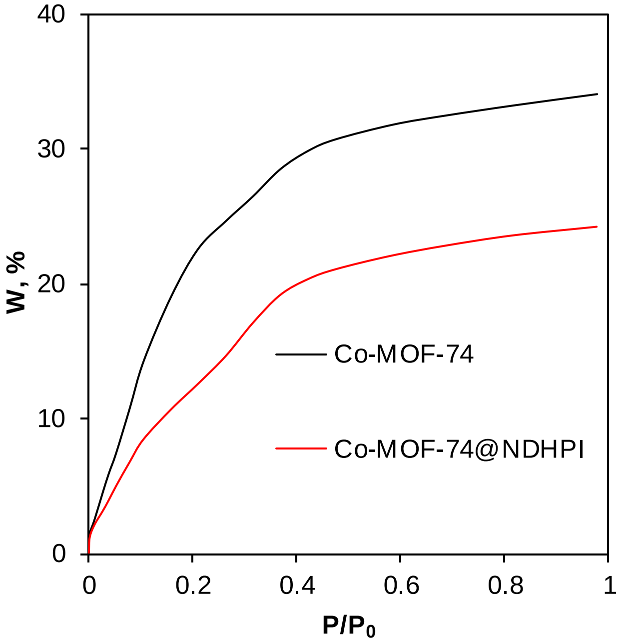

Figure 4. Toluene adsorption isotherms of the samples.

Table 1: BET surface area and pore volume of the samples.

Sample	S_{BET}, m^2/g		V_p, cm^3/g	
	N_2	Benzene	N_2	Benzene
Co-MOF-74	1197	347	0,4	0,2
Co-MOF-74@NDHPI	736	190	0,2	0,1

3.2. Aerobic oxidation of toluene

The results of the solvent-free aerobic oxidation of toluene are presented in Figure 5. Initially, a blank run in the absence of the catalyst was performed, which showed no activity in the solvent-free aerobic oxidation of the toluene. When Co-MOF-74 or NDHPI separately were employed as the catalysts, the reaction proceeded and resulted in 4% and 2% toluene conversion, respectively. The reaction products in those cases were only benzyl alcohol (Bz.OH) and benzaldehyde (Bz.CHO) with no signs of benzoic acid (Bz.COOH). The conversion increased remarkably when Co-MOF-74@NDHPI composite material was applied as a catalyst, the toluene conversion value was 16% along with suitable selectivity on benzoic alcohol and benzaldehyde (18 and 48%) as well as 34% selectivity to benzoic acid, which is significantly higher in comparison with the previously published [12] experimental results on the solvent-free aerobic oxidation of toluene using the Cu-BTC@NHPI catalytic system under similar reaction conditions. In order to evaluate the effect of NDHPI impregnation into Co-MOF-74 on catalytic activity, a control experiment was performed using a physical mixture of Co-MOF-74 and NHPI with the same stoichiometry as in the composite material. The results of the catalytic performance showed a 10% conversion of toluene and similar to the experiments with a single NDHPI and Co-MOF-74 as catalyst product distribution with no traces of benzoic acid. Such a result in the conversion and selectivity can be attributed to the sum of the catalytic effects of the mixture components and indicate the absence of interaction between the NDHPI and Co-MOF-74 in contrast with the composite material Co-MOF-74@NDHPI where the synergistic effect is clearly evidenced. This effect can be explained by the formation of catalytically active complexes between NDHPI and open metal sites in activated Co-MOF-74. The crystal structure of the MOF-74 represents a 1-D honeycomb topology, with pores of 1.1–1.2 nm in diameter. The metal coordination sphere is occupied by six oxygen atoms, one of which comes from a solvent water molecule[21]. By applying heat under a vacuum, one can successfully remove water from the coordination sphere developing coordinatively unsaturated (open) metal sites[23], which can be utilized for further post-synthetic modifications [24]. NDHPI as an analogue of NHPI is able to enter the coordination sphere of cobalt as a ligand, creating catalytically active complexes [25,26]. Thus it is reasonable to speculate that in the case of activated Co-MOF-74, NDHPI with a molecular size of around 0.5x1.1 nm can be accommodated inside the intracrystalline space of the MOF, which favours the increasing oxidation properties of Co-MOF-74.

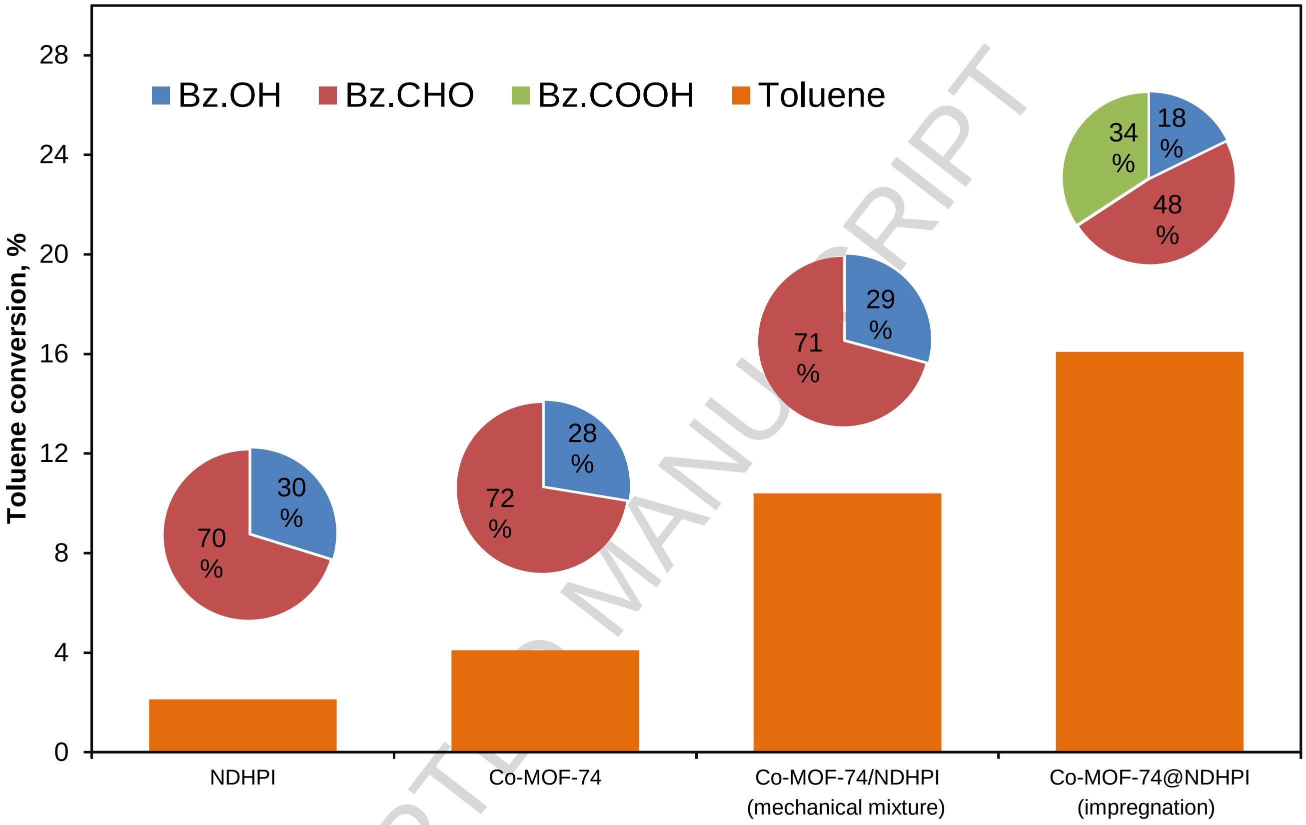

Figure 5. Toluene conversion and product selectivity (circle histograms) obtained after 2 h of oxidation at 100ºC, with O_2 :1.6 MPa using various catalysts.

The structural stability of the recovered Co-MOF-74@NDHPI catalyst was checked. After the first reaction cycle, the catalyst was filtered off, washed with chloroform and oven-dryed at 60ºC for 12h. Obtained sample was investigated with XRD and FTIR techniques. The results are shown in Fig S3 and S4 (supporting information). All characteristic peaks of the used catalysts are well consistent with the fresh ones, indicating excellent stability of the used Co-MOF-74@NDHPI catalyst under reaction conditions.

Conclusions

We have demonstrated that the composite materials based on cobalt metal-organic frameworks containing a guest molecule of multi-nitroxy organocatalyst NDHPI in the intracrystalline space is an effective catalyst for the process of the controlled oxidation of toluene in the absence of additional solvents under mild reaction conditions. The use of cobalt and NDHPI leads to a remarkable enhancement in process efficiency in comparison with previously reported analogues.

Acknowledgement

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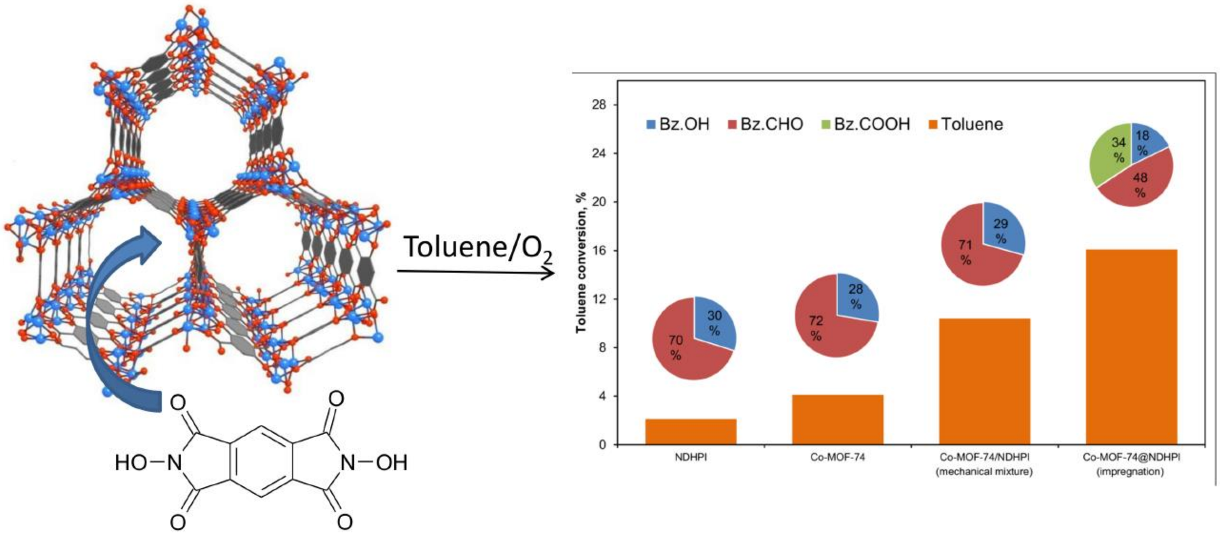
Graphical abstract



Highlights

- Cobalt containing MOF-74 modified with N,N'-Dihydroxypyromellitimide (NDHPI) was synthesized.
- Co-MOF-74@NDHPI was used as catalyst for aerobic oxidation of toluene.
- Impregnation of NDHPI leads to enhancement in oxidation efficiency.
- Impregnation of NDHPI favours the increasing oxidation properties of Co-MOF-74.