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Modification HKUST-1 as a catalyst for the reduction of 4-nitrophenol

Bui Thi Thanh Ha [1], Le Van Duong*[2], Le Ngoc Duong[3], Ta Ngoc Hung[4], Nguyen Le Anh[5] ,Ta Ngoc Don[2]

[1]*Hanoi University of Pharmacy*
[2]*School of Chemical Engineering, Hanoi University of Science and Technology, No. 1, Dai Co Viet, Hanoi*
[3]*Hanoi College of Medicine and Pharmacy*
[4]*Deakin University, Australia*
[5]*High School for the Gifted, Hanoi National University of Education*
[*]*Email: Duong.levan@hust.edu.vn*

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ABSTRACT

HKUST-1 (MOF-199), a metal-organic framework material is synthesized from $Cu(OH)_2$ and modified by Pt. The prepared catalysts were used to reduce 4-nitrophenol (4-NP) into 4-aminophenol (4-AP). Featured results of the catalysts by XRD, SEM, TEM, FTIR, BET, DTA/TGA... showed that metal modified process with reduced agent ethylene glycol had high efficiency, with modified yield up to 90 %. Under our experimental conditions, the catalysts based HKUST-1, containing Pt had high efficiency; conversion was greater than 93 % in reduced reaction of 4-NP. Thus, the catalyst sample contained 2% Pt was the most suitable for the reduction with conversion gained 99,4 % after 250s.

Introduction

HKUST-1 is a Metal-organic frameworks (MOFs) made up of Cu^{2+} ions and 1,3,5-benzene tricarboxylic acid (H_3BTC) linkers in solvents such as ethanol, methanol, water, DMF,... [1-7]. There are many methods to synthesize MOFs materials such as: hydrothermal/ solvent heat [3, 4, 8], microwave [9], ultrasonic [10, 11],... but the solvent heat method is the most commonly used because of many advantages, including a high crystal formation rate, simple implementation and low energy consumption. However, the reaction needs good thermal stability and takes a long time (slow reaction) for crystals to form [11].

With an ordered structure and molecular sized capillary system, HKUST-1 can be used as a catalyst [12-21], gas absorption - separation, gas storage, adsorption [1, 22-32].

In [6], the research team studied the factors affecting the synthesis process and selected the suitable synthesis conditions: temperature below 100 ^oC, 24 hours and environmentally friendly and highly efficient water and ethanol solvents. The synthesis method includes many advantages such as: $Cu(OH)_2$ materials are not too expensive, solvents are environmentally friendly, and the synthesis process is simple.

This paper presents the application of HKUST-1 as a catalyst for the reduction reaction to produce 4-aminophenol (4-AP) - a pharmaceutical precursor for the synthesis of paracetamol [33-38].

There are several methods of 4-AP synthesis such as multi-step reduction of 4-nitro chlorobenzene or 4-

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nitrophenol (4-NP) with acid/iron; hydrogenation catalyzed by 4-NP or nitrobenzene and electrochemical synthesis method. However, the multi-step iron acid reduction process generates a large amount of Fe, FeO sludge, which cannot be reused and causes serious problems in their disposal [33]. In the case of hydrogenation catalyzed by nitrobenzene in a strongly acidic environment, the mixture produced a significant amount of aniline and a small number of other impurities mixed into the product. In addition, the use of highly corrosive mineral acids was a drawback.

There are several methods which have been proposed: i) Hydrogenation of 4-NP in the presence of metal catalysts such as Ni, Pt, and Pd; ii) Reduction of 4-NP by hydrazine in water-ethanol solvent with the presence of a Nickel Raney catalyst [39]; iii) Reduction of 4-NP by using $NaBH_4$ to form 4-AP [40-46]. Among them, the reduction of 4-NP by borohydride in the presence of suitable catalysts is an attractive option because the low toxicity of borate makes borohydride relatively easy to use, environmentally friendly and the reduction of 4-NP can be easily observed by color change from yellow to colorless (on UV-Vis spectroscopy) [31, 40]. The isobaric points in the spectrum of the reaction mixture demonstrated that no byproducts were formed [40, 42].

In the absence of a catalyst, the reaction did not occur even after 2 days [41], however, in the presence of metal nano catalysts, the reaction proceeded easily. Metal-containing catalysts have been reported with high efficiency such as: crystalline Pd-Ag, nano-Ag immobilized in microgel cores, nano-Ag immobilized on highly branched polymer fibers, and nano-Pt immobilized on Spherical polymer brushes (SPB), Pd nano stabilized on chitosan and Au, Ag, Cu nano [40-46].

Because MOFs in general and HKUST-1 in particular do not have very high thermal stability, the metal transfer process does not use heating and reduction in high temperature methods. The research team carried out the metal salting process simultaneously with the reduction process using ethylene glycol solvent as the reducing agent. Some factors affecting catalysis modification process and the reaction process had also been studied to select the suitable conditions for the catalyst fabrication process.

Experimental

Materials

The starting materials were $Cu(OH)_2$ (pure, China) and 1,3,5-benzene tricarboxylic acid (H_3BTC, 95 % Sigma, USA) and $NaBH_4$ (96 %, China). The 0.01M H_2PtCl_6 and 0.01M $PdCl_2$ solutions were produced from Sigma's pure chemicals (USA). Solvents such as ethanol (EtOH, 99.5 %, China), ethylene glycol (EG, 98 %, China), double distilled water were produced in the laboratory.

Catalytic reduction of 4-NP

HKUST-1 was synthesized according to [6]: reaction mixture with appropriate ratio: $Cu(OH)_2$: H_3BTC: EtOH: H_2O = 9: 7,2: 10: 20 (mmol : mmol : ml : ml). The reaction mixture was crystallized at 75 °C for 24 h, without stirring. At the end of the reaction, the samples were naturally cooled down to room temperature, filtered and washed three times with water and ethanol, and dried under vacuum at 120 °C for 6 hours. Impregnating metal on materials: 1 ml of 0.01 M H_2PtCl_6 solution was mixed with 10 ml of ethylene glycol and 0.2 g of HKUST-1 to get a suspension. Ultrasonic vibration of the suspension mixture was conducted for 1 min, then the flask containing the suspension mixture was mounted on a magnetic stirrer with a condenser; refluxing and heating to 120 °C were carried out for 4 h, obtaining HK-Pt 2%. These steps were repeated to get a catalyst containing 0.5% Pt, 1% Pt, 3% Pt (theoretical content of transition metals). The corresponding 0.01 M $PdCl_2$ solution was substituted to obtain a catalyst containing 1% Pd. The catalytic recovery efficiency was calculated based on the mass of the product obtained compared with the initial mass of HKUST-1. Impregnation efficiency was expressed as % metal content (according to EDX) compared with % theoretical content in the catalytic product after modification.

Catalytic Activity Test

The reduction of 4-nitrohenol reaction was carried out in cuvettes, similar to [48-54]: 1 ml of 0.025 M $NaBH_4$ and 2.4 ml of 0,1 x 10^{-3} M 4-nitrophenol solution were added to the cuvette. (Molar ratio $NaBH_4$/4-NP ≈ 100). 30 µl HKUST-1 catalyst suspension (concentration 5 mg/ml) was added, and the absorbance of the solution was measured.

Characterization techniques

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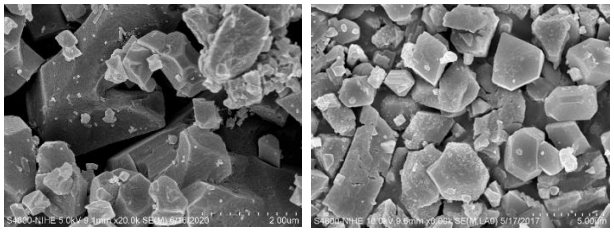
The X-ray diffraction pattern was recorded on a D8-Brucker machine (Germany), using Cu X-ray tube with wavelength CuK_α = 1,54056 Å, voltage 40 KV, amperage 40mA, temperature 25 °C, with a scan speed of 0,02 °/s. SEM images were taken on a Field Emission Scanning Electron Microscope S-4800. Samples were taken TEM on JEM 1010 machine with resolution 2 Å, voltage 100 kV. Specific surface area and pore volume were determined on Micromeritics Gemini VII 2390 (USA). EDX spectra were recorded using a JED-2300 Analysis Station at the Institute of Materials Science, Vietnam Academy of Science and Technology. The UV-Vis analysis was done on an Agilent UV-Vis machine at the laboratory of the Institute of Chemical Engineering, Hanoi University of Science and Technology.

Results and Discussion

Metal modification based on material HKUST-1

Determination of modified metal

The modification results were clearly shown in SEM images. XRD diagrams of two samples HK-Pd 1% and HK-Pt 1% respectively were presented in Figure 1 and Figure 2. In Figure 1a, the structure of the HKUST-1 had been significantly broken; the particle size was no longer uniform. In Figure 1b, it could be seen that the HKUST-1 based material structure was not destroyed. This can be explained by the fact that the modified environment by $PdCl_2$ was more acidic, and disrupted the HKUST-1 structure more.



(a) (b)

Figure 1: SEM images of HK-Pd 1% (a) and HK-Pt 1% (b)

Similarly, as observed from 2 XRD histograms of 2 samples HK-Pd 1% (Figure 2a) and HK-Pt 1% (Figure 2b), it could be clearly seen that both of these samples contained only 1 set of HKUST-1. The main difference was that the characteristic peak of HKUST-1 in the HK-Pt 1% sample was much stronger than that of the 1% HK-Pd sample. At the same time, the 1% HK-Pt sample had a lower baseline than the 1% HK-Pd, which meant that the amorphous amount in the 1% HK-Pd sample was more than that in the 1% HK-Pt, which was consistent with the following catalytic recovery efficiency. The calculated metal modification for HK-Pt 1% sample (equivalent to 88.2 %mass) was much higher than that of HK-Pd 1% (equivalent to 48.2 %mass).

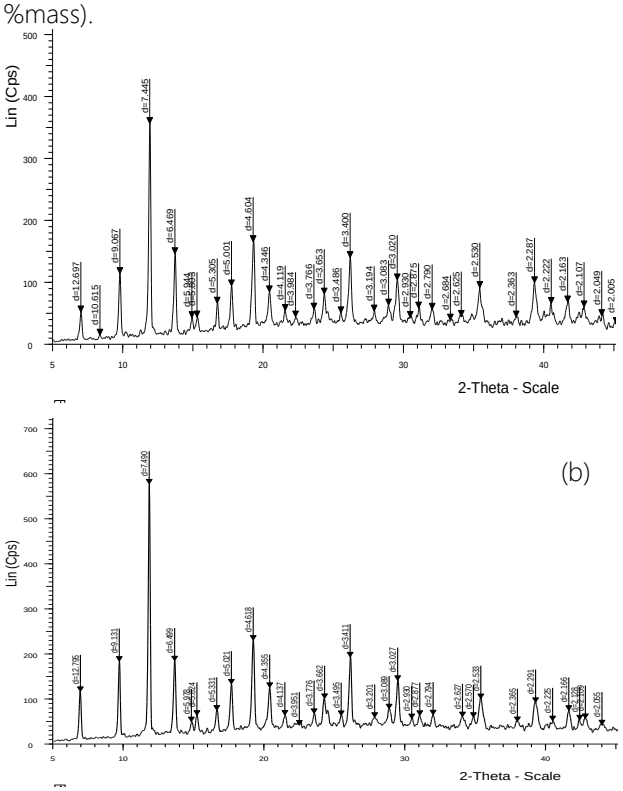


Figure 2: XRD patterns of HK-Pd 1% (a) and HK-Pt 1% (b)

Thus, the Pt modified material on the basis of HKUST-1 showed that the original structure of HKUST-1 remained intact and had high catalytic efficiency, so Pt will be selected for the subsequent modification processes.

Determination of modification temperature

Three samples were modified with Pt (1% theoretical Pt content) at temperatures of 100, 120 and 150 °C with the results given in Table 1.

Table 1: Results of HKUST-1 modification with Pt at different temperatures

Sample	Modification temperature, °C	Pt content according to EDX % mass	Product recovery efficiency % mass
HK-Pt-100	100	0,28	89,5
HK-Pt-120	120	0,53	88,2
HK-Pt-150	150	0,85	25,6

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The results presented in Table 1 showed that, under the same experimental conditions, when increasing the modification temperature from 100 to 120 and 150 °C, the content of Pt impregnated on HKUST-1 sample increased gradually from 0.28 to 0.53 and 0.85 % according to EDX, but the yield of HKUST-1 after modification gradually decreased and decreased very strongly when HKUST-1 was modified at 150 °C (89.5; 88.2 and 25.6 % respectively).

The results above showed that increasing the modification temperature reduced the viscosity of EG and increased the dissolution rate of Pt^{4+} in EG, rapidly increased the HKUST-1 surface approach process, and increased the Pt content in HKUST-1 after modification. However, at a temperature of 150 °C, the obtained HKUST-1 structure was strongly broken and dissolved in the solution, so after treatment, the HKUST-1 recovery efficiency was only 25.6 % compared to the original. The modified sample at 120 °C was considered to be the best of the 3 samples studied, so the modification temperature chosen for upcoming studies was 120 °C.

Determination of modification time

The results of three HKUST-1 modified samples with Pt (2% theoretical Pt content) at 120 °C for 2, 4 and 6 hours were presented in Table 2.

Table 2: Results of HKUST-1 modification with Pt at different times

Sample	Modification time, hours	Pt content according to EDX, % mass	Product recovery efficiency, % mass
HK-Pt-2h	2	0,36	86,1
HK-Pt-4h	4	1,79	86,6
HK-Pt-6h	6	1,87	82,6

When increasing the modification time from 2 hours to 4 hours, the Pt content in the obtained catalyst sample increased sharply from 0.36 to 1.79 %. When the modification time was futher increased to 6 hours, the Pt content only increased slightly to 1.87 %. Meanwhile, the highest product yield (88.2 %) corresponded to the impregnation efficiency of 86.6 % when the modification time was 4 hours. It can be explained that the reducing factor EG was not strong, so the rate of reduction reaction was slow.

In the first 2 hours, the process of dissolution and adsorption of Pt^{4+} mainly occurred; there was not enough time for Pt^{4+} to bind and disperse evenly on the surface of the material and the reduction reaction was incomplete as well, with the result that Pt content only reached 0.36 % by mass. However, if the reaction time was extended to 6 hours, although the Pt content was increased, it was not much higher, which reduced the HKUST-1 yield after modification possibly due to partially broken HKUST-1 structure and dissolved in solution. Therefore, a suitable modification time at 4 hours was recommended for the next study.

Effect of Pt content on 4-NP reduction reaction

Results of 4 modified samples of HKUST-1 with Pt at the rate of 0.5; 1; 2 and 3 % mass at 120 °C for 4 hours were shown in Table 3. The results in Table 3 show that when HKUST-1 samples were modified with Pt at different concentrations (from 0.5 to 3 %), the yield of HKUST-1 obtained after modification tended to decrease gradually (from 89.1 to 72.7 %).

Table 3: Results of HKUST-1 modification with different concentrations of Pt

Sample	Product recovery efficiency, % mass	Theoretical Pt content, % mass	EDX content of Pt, % mass		
			mark 1	mark 2	medium
HK-Pt 0.5%	89,1	0,5	0,37	0,10	0,23
HK-Pt 1%	88,2	1	0,51	0,54	0,53
HK-Pt 2%	86,6	2	1,80	1,78	1,79
HK-Pt 3%	72,7	3	2,35	2,56	2,45

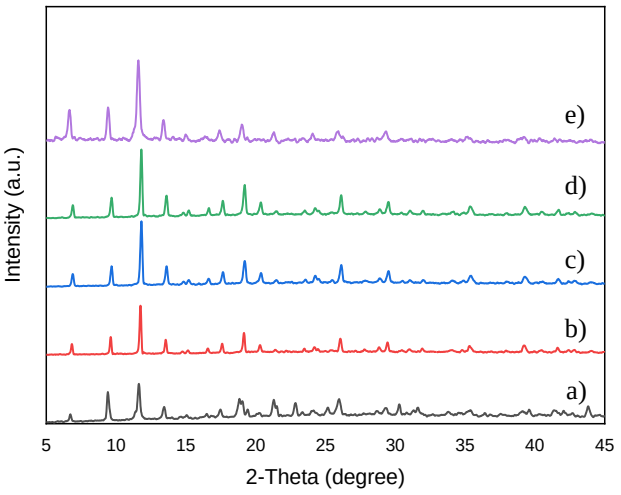

Figure 3: XRD patterns of the HK-Pt 3% (a); HK- Pt 2% (b), HK-Pt 1% (c), HK-Pt 0,5% (d) and HKUST-1 (e)

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This result proved that, under the same reaction conditions, when the Pt content was increased gradually i.e., more H_2PtCl_6 was used, the reaction environment could be more acidic, thus breaking HKUST-1 structure more. This broken HKUST-1 structure was mainly dissolved in solution, thus reducing the amount of HKUST-1 solids after modifcation. There was also a part in the amorphous form. This was also confirmed by the XRD diagram shown in Figure 3.

Observing the XRD pattern of 4 samples of modified HKUST-1 with different Pt contents in Figure 3, it was clearly showed that all 4 XRD diagrams contain only a single HKUST-1 crystalline phase, but had different characteristic peak intensities and baselines. If HKUST-1 sample before modification (Figure 3e) had a characteristic peak at 2θ ≈ 11,6° with the highest intensity, when this sample was modified with Pt content increasing gradually from 0.5 to 1.0 and 2.0 % (respectively in Figures 3d, 3c and 3b), X-ray diffraction with a characteristic peak at 2θ ≈ 11,6° with decreasing intensity was obtained, showing that the HKUST-1 crystallinity also decreased. The HKUST-1 sample modified with the highest Pt content (3 %, figure 3a) had the lowest peak intensity at 2θ ≈ 11,6° and the highest baseline among the four samples, showing that this sample had lowest crystallinity.

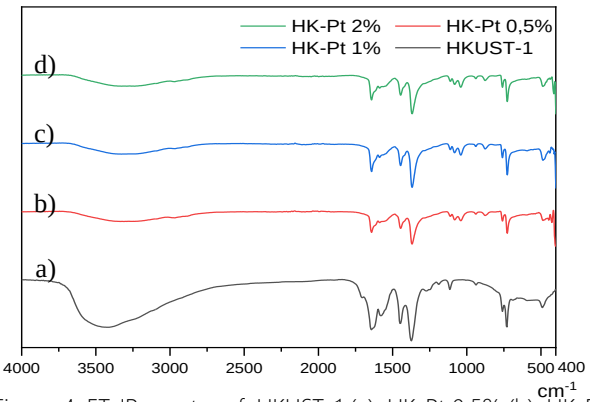

Figure 4: FT-IR spectra of: HKUST-1 (a), HK-Pt 0.5% (b); HK-Pt 1% (c) and HK-Pt 2% (d)

FTIR spectra of HKUST-1 sample impregnated with Pt (Figure 4) with different amounts still had almost identical spectral clusters, confirming the similar chemical topology and retaining the structure of HKUST- 1.

The results of thermal analysis in Figure 5 showed that when impregnation of metal Pt was carried out on HKUST-1, the thermal stability of the sample decreased, and two samples HK-Pt 1% and HK-Pt 2% had exothermic peak reaching the extreme. The extremes were at 326 °C and 320 °C respectively, corresponding to the decomposition of the HKUST-1 structure impregnated with Pt to produce CuO under the influence of O_2 in the air. The DTA/TGA diagram also showed that the total weight loss of HKUST-1 sample while heated modified with Pt at the ratio of 1 and 2 %, respectively, was 77.9 % and 77.2 %, which was very high, indicating that the following sample when modified Pt impregnated still had a large porosity.

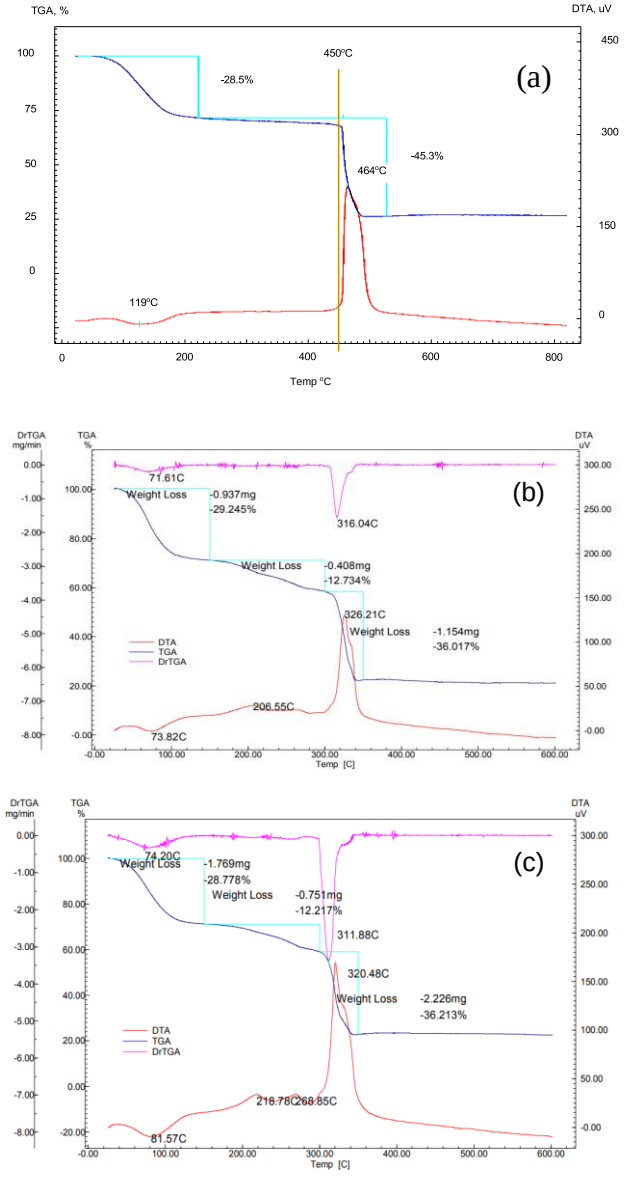

Figure 5: TGA-DTA diagram of: HKUST-1 (a), HK-Pt 1% (b) and HK-Pt 2% (c)

The SEM images of the samples impregnated with Pt (HK-Pt 1%, HK-Pt 2%) in Figure 6 showed that the samples still had the characteristic crystalline grains of HKUST-1. In the meantime, there were many small adherent particles that were regarded as Pt atoms on the surface. The TEM image of the 2% HK-Pt sample also clearly showed metal particles on the surface of

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the material. It is possible that these were Pt or Cu metal particles which were reduced and attached to the crystal. Thus, they could be the catalytic sites for the reduction reaction in the presence of hydrogen.

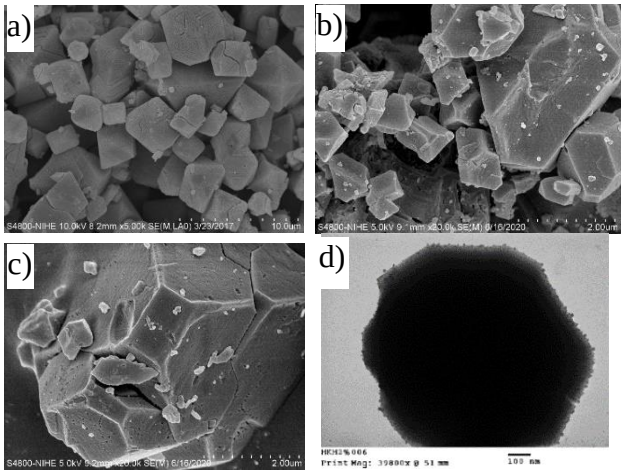

Figure 6: SEM images of HKUST-1 (a), HK-Pt 1% (b); HK-Pt 2% (c) and TEM image of HK-Pt 2% (d)

The distribution of Pt content at different points on the surface tested by the EDX method, was listed in Table 4. The 0.5% Pt impregnated sample had an uneven distribution of Pt on the surface among points while 1% Pt impregnated samples had low impregnation efficiency at only 53 %. If the Pt content was added theoretically to 2 % and 3 %, then the Pt impregnation efficiency on HKUST-1 material increased sharply. Indeed, the 2% Pt impregnated sample had the highest impregnation efficiency (reaching 89.5 %) and the product yield was also high (reaching 86.6 %).

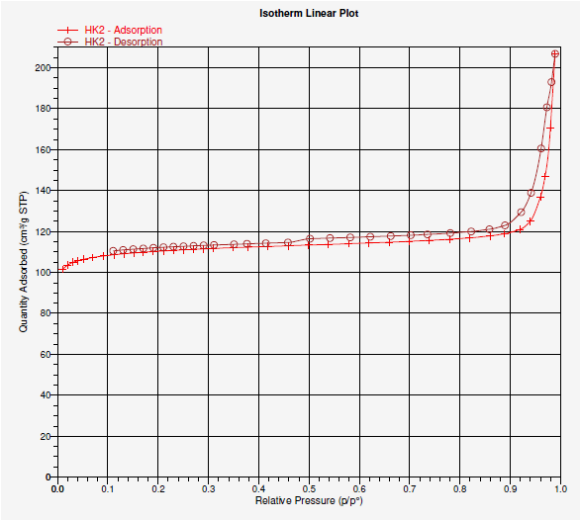

Figure 7 : N_2 adsorption - desorption diagram of HK-Pt 2%

The HKUST-1 sample impregnated with 2% Pt was also measured for N_2 adsorption-desorption to determine the specific surface area and pore volume (Figure 7). The results showed that the specific surface area of the HK-Pt 2% sample according to BET was quite high, reaching 370 m^2/g and the microcapillary volume was 0.162 cm^3/g.

The corresponding data of HKUST-1 sample before modification with Pt at 1,468 m^2/g, 219 m^2/g and 0.555 cm^3/g showed that although impregnation of Pt to HKUST-1 sample did not change the structure, it drastically reduced the surface area and microcapillary volume due to the presence of Pt on the surface (both inside and outside the capillary). Hence, it reduced the microcapillary volume leading to a sharp decrease in the surface area. Notably, the HK-Pt 2% sample with adsorption band and lines with late ring, indicated that after modification with 2% Pt there was an average capillary appearance that the original HKUST-1 sample [6] did not have. The average capillary appearance was due to the appearance of the gap between the HKUST-1 crystal grain clusters after Pt was distributed on the surface of the material.

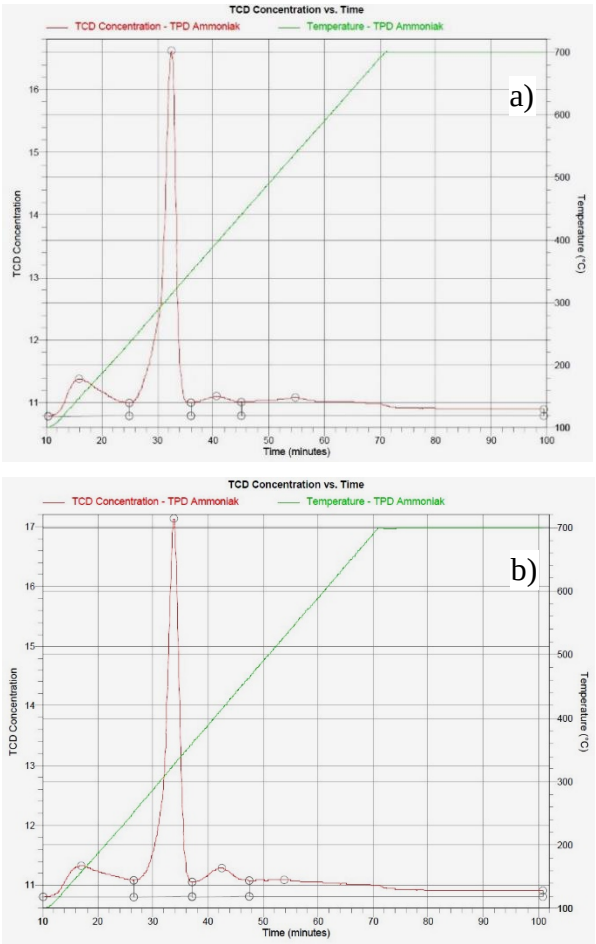

Figure 8: TPD-NH_3 diagrams of HK-Pt 2% (a) and HK-Pt 1% (b)

The TPD-NH3 diagrams (Figure 8) of the HKUST-1 catalyst samples impregnated with Pt (1 % and 2 %) and the original HKUST-1 sample [6] were similar; they

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mainly contained moderate acid centers and concentrated around 313 and 333 °C, in addition, there were some weak acid centers around 147 and 157 °C while they contained only very few strong acid centers around 528 and 538°C. With these acid centers, while conducting the reaction at low temperature and especially in an alkaline environment such as the 4-nitrophenol reduction reaction with $NaBH_4$ it could be less affected; hence they were suitable for this reaction. However, the sample HK-Pt 2% had the most uniform distribution of Pt on the surface of the material and gave the highest post-modification efficiency as discussed from the results in Tables 3.9 and 3.10. Thus, this sample was considered suitable when using as a catalyst for the reduction reaction from 4-NP to 4-AP.

Result of 4-NP reduction reaction

The 4-NP solution in water showed an absorption peak at 317 nm (Figure 9). When $NaBH_4$ was added, the alkalinity of the solution increased (pH increased) which converted to 4-nitrophenolate (4-NP^-) ions along with a spectral shift with absorption peaks moving to 400 nm [38]. The color of the solution changed from light yellow to dark yellow (4-NP+ $NaBH_4$ sample). On the other hand, for the samples with the addition of HKUST-1 catalyst, the absorption sugar was reduced because the catalyst could partially adsorb 4-NP; but it was worth noting that the absorbance at the 400 nm position of the $NaBH_4$+Cat and the $NaBH_4$+Cat samples 4-NP+Cat was almost equivalent, indicating that the catalyst has little absorption of this wavelength. The study results of the reduction reaction of 4-NP will use the absorbance at 400 nm to calculate the reduction reaction conversion [34, 37, 40-42, 46].

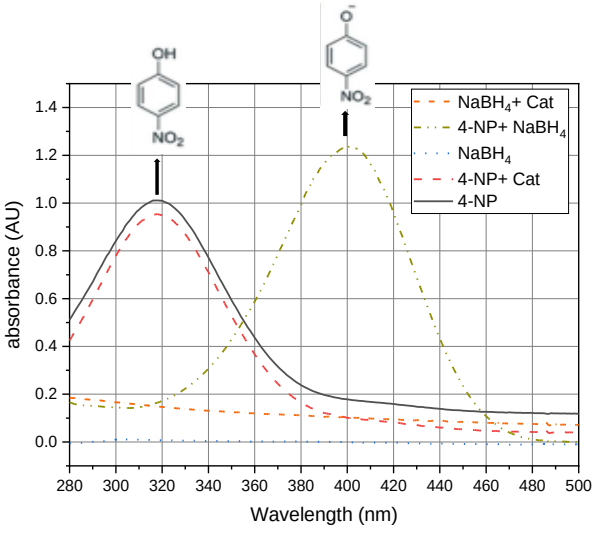

Figure 9: UV-Vis spectra of the starting solutions

Without an additional catalyst, the mixture could retain the yellow color and the absorbance at 400 nm could be almost unchanged (Figure 10). The conversion of the reduction reaction was only 2.1 %. It showed that the reduction reaction would be almost impossible without a catalyst. This is also consistent with the research by [34, 37, 40].

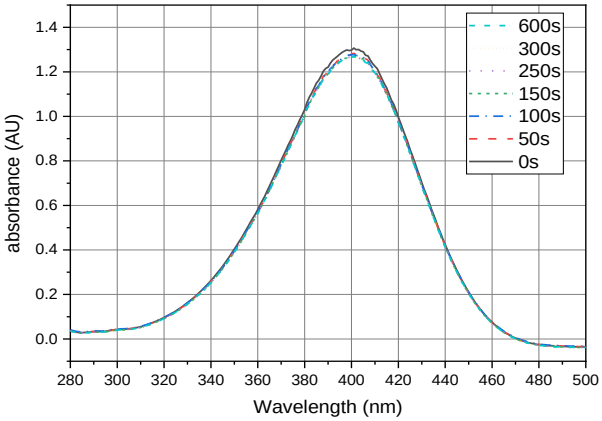

Figure 10: UV-Vis spectrum of (4-NP+$NaBH_4$) without catalyst

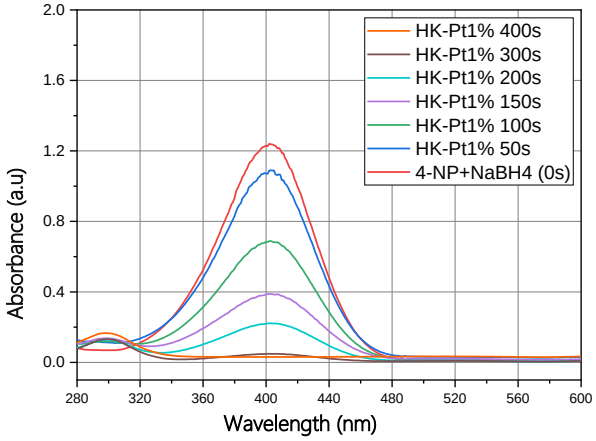

Figure 11: UV-Vis spectrum of (4-NP + NaBH4) in the presence of HK-Pt 1% catalyst

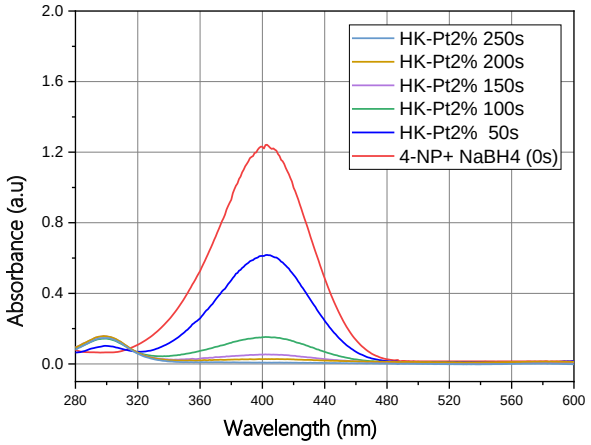

Figure 12: UV-Vis spectrum of (4-NP + NaBH4) in the presence of HK-Pt 2% catalyst

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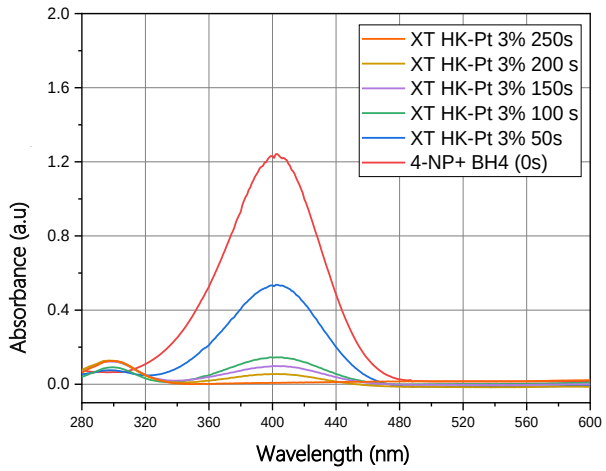

Figure 13: UV-Vis spectrum of (4-NP + NaBH4) in the presence of HK-Pt 3% catalyst

The results of the usage of HKUST-1 catalyst impregnated with Pt 1%, 2% and 3%, were depicted in Figures 11, 12, 13 respectively. If HK-Pt catalyst was added, the intensity peak at the 400 nm wave region, which was characteristic for 4-NP-, decreased rapidly while the intensity peak at 300 nm increased corresponding to the generation of 4-aminophenol (4-AP).

After the first 100s, the 1% Pt catalyst only had a conversion rate at 44.3 %, but after 300s the conversion rate reached 96.1 % and after 400s at 97.5 %. In addition, the peak at the 400 nm wave decreased rapidly in 2% Pt catalyst; 50.3 % 4-NP was converted before 50s. Furthermore, after 200s the conversion rate reached 97.8 %. Eventually, after 250s, the reaction was almost finished when 99.4 % 4-NP was converted to 4-AP. Besides, the reaction also occurred very quickly using HKUST-1 catalyst impregnated with 3% Pt; the conversion reached 56.7 % in the first 50s and more than 98.8% after only 250s.

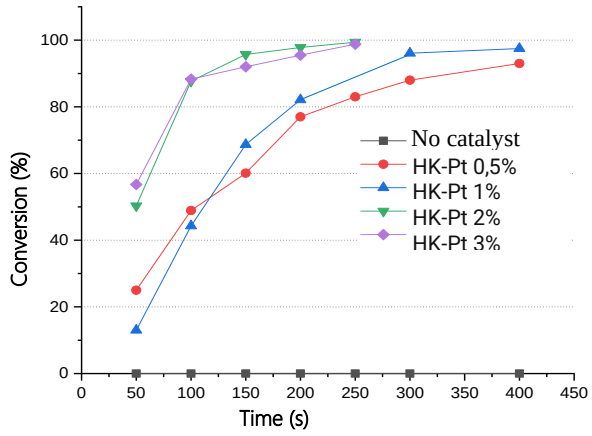

Figure 14: 4-NP conversion degree of HKUST-1-based catalysts with different Pt contents

As shown in figure 14, the graph of HKUST-1 catalysts impregnated with Pt had a large slope at the beginning and a high conversion rate. Thus, the graph clearly showed that the reaction rates of the catalyst samples based on HKUST-1 were high. The HKUST-1 catalyst sample impregnated with 0.5% Pt also had the conversion rate over 80 % after 250s and 93 % after 400s.

These results are suitable with the Langmuir - Hinshelwood kinetic model [46]: both reactants (4-NP- and BH4-) needed to be adsorbed on the surface of the catalyst, when the concentration reached the appropriate value, and the reaction could take place. The 0.5% HK-Pt sample in the first 100s also had a higher conversion rate than the 1% HK-Pt sample possibly because the porous material had good adsorption. On the other hand, the two samples HKUST-1 impregnated with 2% and 3% Pt both had high conversion and reaction rates because of the good adsorption capacity due to the large specific surface and there being also many Pt metal centers that support the promotional response reaction faster. In addition, the sample HK-Pt 2% used less Pt but still had the same efficiency, so it was selected as a suitable catalyst sample for the coming reduction reaction studies.

Conclusion

The catalyst was synthesized on the basis of HKUST-1 impregnated with 0.5-3% Pt (theoretically), and the suitable sample was selected as HK-Pt 2% with Pt impregnation efficiency of 89.5% and the recovery efficiency of catalytic product after impregnating reached 86.6%. The catalysts characterized by modern physicochemical methods showed that the catalyst retained the porous structure of HKUST-1, had good thermal stability, and met the requirements of a catalyst for the reduction reaction.

The 4-NP reduction reaction has been studied on the prepared Pt-containing catalysts; the results showed that the metal-impregnated catalyst samples on the basis of HKUST-1 were highly effective in the 4-NP reduction reaction. In addition, the HK-Pt 2% sample impregnated theoretically with 2% Pt (1.79% Pt by EDX) had the highest efficiency with the conversion of 4-NP to 4-AP reached 99.4% after 250s.

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