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Study on the characteristics and catalytic properties of Pt/SBA-15 in the selective oxidation of D-Glucose

Tran Thi Nhu Mai*, Nguyen Thi Minh Thu, Pham Dinh Trong, Nguyen Thi Ha, Giang Thi Phuong Ly

Faculty of Chemistry, Hanoi University of Science, VNU, 334 Nguyen Trai, Hanoi, Vietnam

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Abstract. In this work, platinum nanoparticles were dispersed on SBA-15 mesoporous material by incipient wetness method and the synthesized materials were characterized by XRD, TEM, EDX spectroscopies and N_2 adsorption-desorption isotherm measurement.

The results indicated that 2D hexagonal ordered structure of SBA-15 was still maintained after grafting Pt on SBA-15 support and platinum nanoparticles existed both inside and outside the pore channels of SBA-15 material. Catalytic activity of these materials was tested in the aqueous phase D-glucose oxidation as a model reaction. The reaction was carried out in a glass reactor at atmospheric pressure, 80°C, air flow rate 20ml/minute, at pH 9. The results from HPLC-RID method showed that the pH has a profound effect in the platinum-catalyzed oxidation of glucose and high conversion of D-glucose with the highest selectivity to D-gluconic acid was performed with 1%Pt/SBA-15 catalyst.

1. Introduction

Gluconic acid and its salts are important industrial products, they are used as water-soluble cleansing agents or additives in foods and beverages. For commerical purposes, these products are exlusively prepared by the oxidation of glucose or glucose-containing raw materials. Althrough the currently used oxidation method is based on biochemical tranformation but recent development has indicated that the catalytic route may be valid alternative for producing gluconate on an industrial scale. For this reason, many interested reseachs in order to discover the active catalyst for this process have been taken out. In this paper, Pt/SBA-15 materials with various Pt loading on high surface area siliceous support were prepared and tested in D-glucose oxidation process. The properties of these materials were characterized by XRD, TEM, EDX, and N_2 adsorption-desorption methods and the products of the oxidation reaction were determined to estimate the effect of Pt contents, pH and catalysts' nature on the reaction conversion and gluconic acid selectivity.

* Corresponding author. Tel.: 84-4-38261857.
E-mail: tranthinhumai@hus.edu.vn

2. Experimental

2.1. Catalyst preparation

Synthesis of SBA-15: 1g of Pluronic P123 triblock copolymer (E020P070E020, BASE U.S.) as structure-directing agent was dissolved in 75 ml of 1.5 M HCl , and then 2.1g of tetraethylortho-silicate (TEOS) as silicon source was added under strong magnetic stirring at 50°C for a day. The solution was aged for another day at room temperature. After filtration, washing with distilled water and drying at 100°C, the sample was calcined at 550°C in ambient air for 5h and the white SBA- 15 was obtained.

Synthesis of Pt/SBA-15: Platinum was supported on SBA-15 mesoporous material by incipient wetness method using calculated content of H_2PtCl_6 5.10^{-3}M. The heterogeneous mixture was refluxed at 75°C for 3 hours and continuously stirred. $NaBH_4$ solution in ethanol was dropped slowly to reduce all platinum salt to the metallic state. The suspension was filtered, washed several times with distilled water, dried at room temperature overnight and then at 90°C in 5 hours and the light yellow sample of Pt/SBA- 15 was obtained.

Platinum was supported on SBA-15 with Pt various contents (% wt): 1% Pt/ SBA -15 (signed **PS -1**), 2% Pt/ SBA -15 (signed **PS -2**), 3% Pt/ SBA -15 (signed **PS -3**)

2.2. Instrumentation

X-ray Diffraction (XRD) spectroscopy was performed on a SIEMENS D5005 spectrometer (CuKα, wavelength λ= 1,540 Å, voltage 40kV, current 30mA, at room temperature with a scan speed of 0.2°/minute in a 2θ range of 0-40°. High resolution transmission electron microscopy (HR-TEM) was carried out on JEOL-JEM 1010 instrument with voltage 80,0kV and on HITACHI H-7100 Electron microscope with voltage 100,0kV, Direct Mag: 600000x(**Japan Advanced Institute of Science and Technology**). N_2 adsorption-desorption method and Energy Dispersive X-ray Spectroscopy (EDX) were measured on Micromerictics ASAP 2010 and Varian Vista Ax apparatuses, respectively.

2.3. Oxidation procedure of D-Glucose

The reaction was carried out in liquid phase with the presence of oxygen in air, at the range of temperature 50-90°C. The pH value was maintained at 9 and air flow was controlled by Flow Meter 110 AC device. The products of the oxidation was determined by High performance liquid chromatography method (HPLC) with refractive index detection (RID).

3. Results and discussion

3.1. Characteristics of SBA-15 material

The low-angle XRD patterns of SBA-15 at different aging time (24, 48 and 72 hours) as showed in Fig.1 are similar and all show a prominent peak at 2θ=0.9-1° and two weak peaks around 2θ=1.5-2°, which could be indexed as (100), (110), and (200) planes. This is the characteristic hexagonal mesoporous structure of the SBA-15 matrix associated with P6mm symmetry group [3]. The increase of aging time from 24 to 72h leaded to the increase of *d*-spacing between the planes (100) from 88.62 Å (24h) to 93.87Å (48h) and 97.43Å (72h). In these XRD patterns, we also see that two weak peaks indexed as (110) and (200) diffractions of 24h sample are not clear and the intensity of these peaks increases in accordance with aging time, this means that the order of SBA-15 is not enough high at shorter time treatment.

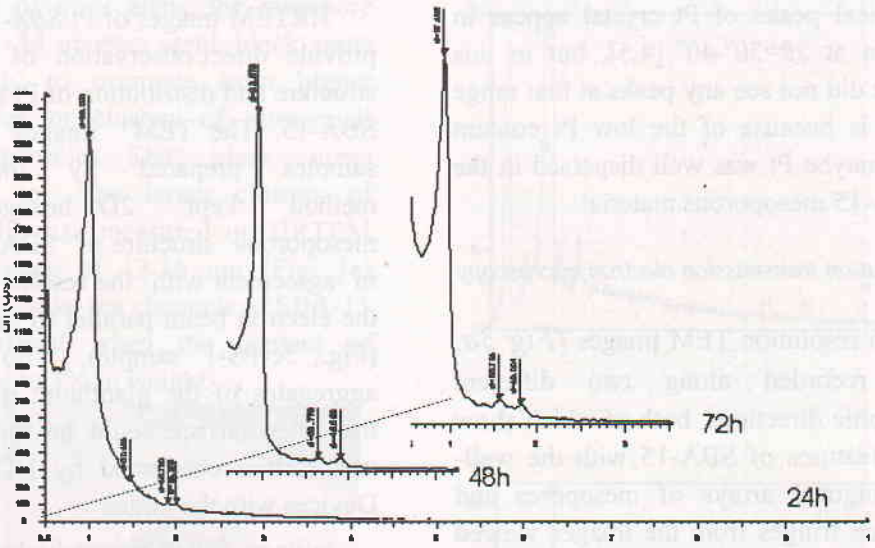


Figure 1. Low-angle XRD patterns of SBA-15 at different aging time (24, 48 and 72 hours).

3.2. Characteristics of Pt/SBA-15 materials

a. X-ray powder diffraction

XRD patterns (Fig.2) of PS-1, PS-2 và PS-3 samples display three peaks of (100), (110), and (200) diffractions in agreement with 2θ angles ~ 0.9^0, 1.7^o, 1.9^o, respectively. All peaks are very obvious which indicate that the modified materials have high order structures and the introduction of Pt did not affect the hexagonal structure of SBA-15 support material [3].

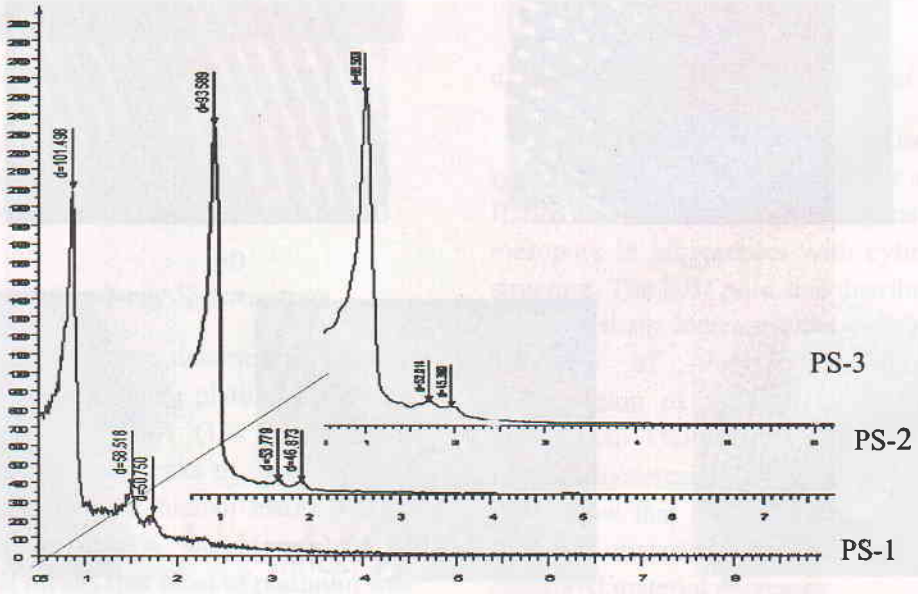


Figure 2. X-ray diffraction patterns of PS-1, PS-2 and PS-3 samples.

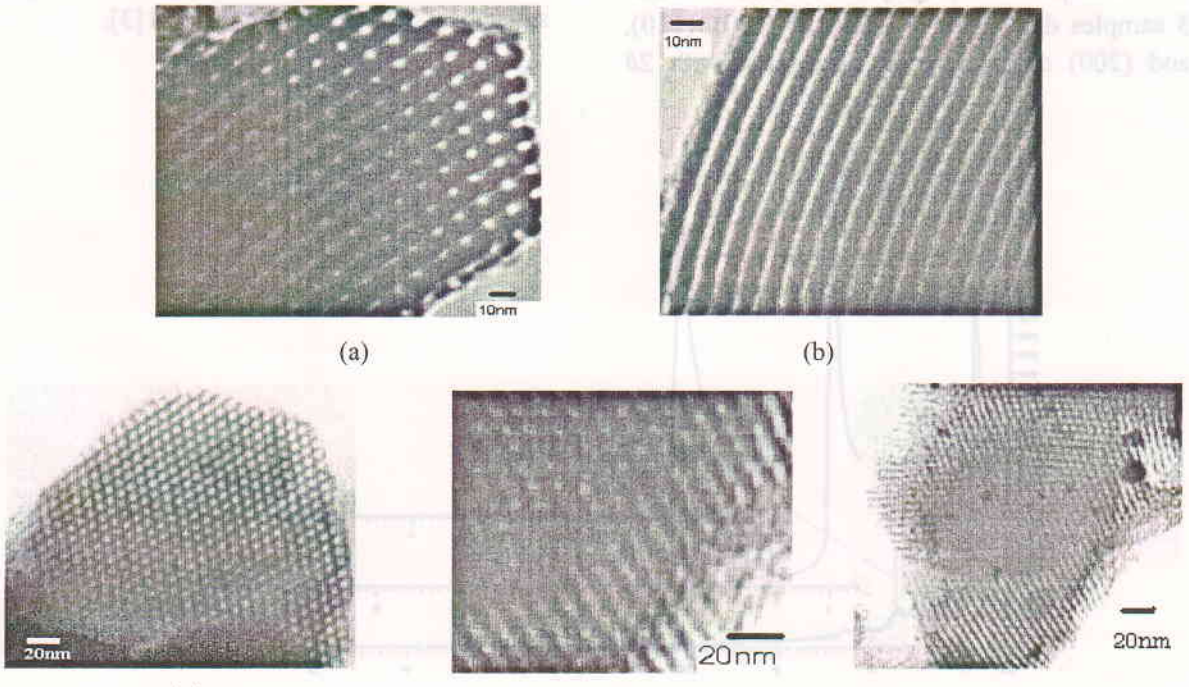
The typical peaks of Pt crystal appear in XRD pattern at 2θ=30°-40° [4,5], but in this research, we did not see any peaks at that range angle. This is because of the low Pt content (<5%) and maybe Pt was well dispersed in the pore of SBA-15 mesoporous material.

b. High resolution transmission electron microscopy

The high resolution TEM images *(Fig 3a, b)* were recorded along two different crystallographic directions, both of which show the typical features of SBA-15 with the well-ordered hexagonal arrays of mesopores and straight lattice fringes from the images viewed along and perpendicular to the pore axis, confirming the existence of a 2-D hexagonal structure of a p6mm symmetry. The distance between two pore centres is about 6nm and the high wall thickness (6-7nm) is beneficial to thermal and hydrothermal stabilities of SBA-15 synthesized material.

HRTEM images of Pt/*SBA*-15 (Fig 3c, d, e) provide direct observation of regular channel structure and distribution of Pt nanoparticles in SBA-15. The TEM images show that all samples prepared by incipient wetness method kept 2D hexagonal ordered mesoporous structure of SBA- 15, which is in agreement with the results of XRD. With the electron beam parallel to the pore channels (Fig. 3c-PS-1 sample), no obvious bulk aggregates of the plantinum metal species on the outer surface could be found. This result was further confirmed by HITACHI H-7100 Devices with the higher

voltage 100,0kV and higher magnification 0f 600.000x(Fig 4). This proved that Pt was dispersed with nano sizes (<6nm) inside the pore of SBA-15 mesoporous material. At this size, Pt shows high performance for many chemical conversions [4-6].



(a) (b) (c) (d) (e)

Figure 3. Transmission electron micrographs of SBA-15 in the direction of pore axis (a)(100) and in the direction perpendicular to the pore axis SBA-15 (b) (110); PS-1 (c); PS-2 (d) and PS-3 (e).

TEM image of PS-2 along the mesopore channels in Fig. 3d appears some black spots which are likely to originate from bigger platinum particles or clusters of ultra-small plantinum nanoparticles. The black areas corresponding to the larger clusters of platinum with the size measured on HRTEM micrograph at range of 12-15 nm (Fig. 3e) were dispersed outside the channels of SBA-15 mesoporous material when the content of platinum increase to 3% in weight.

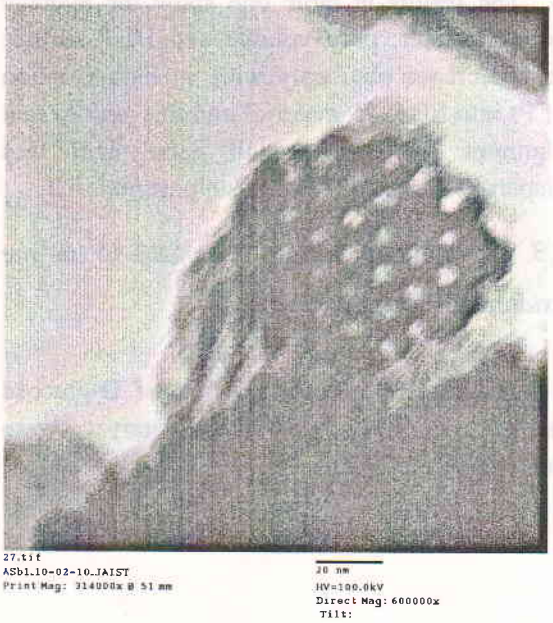


Figure 4. Transmission electron micrographs of Pt/SBA-15(PS-1) in the direction of pore axis (a) (100), HV= 100 kV, Direct Mag: 600.000x

c. Energy Dispersive X-ray Spectroscopy

The content of Pt was determined again by EDX method after reducing platinum salt with NaBH4. Figure 5 of PS-1 (1% Pt/ SBA-15) sample displays typical peaks of Si and Pt and the result from the quantitative estimation of peak areas gives 0,98% weight content of platinum. This means that most of platinum was reduced and maintained on SBA-15 support material.

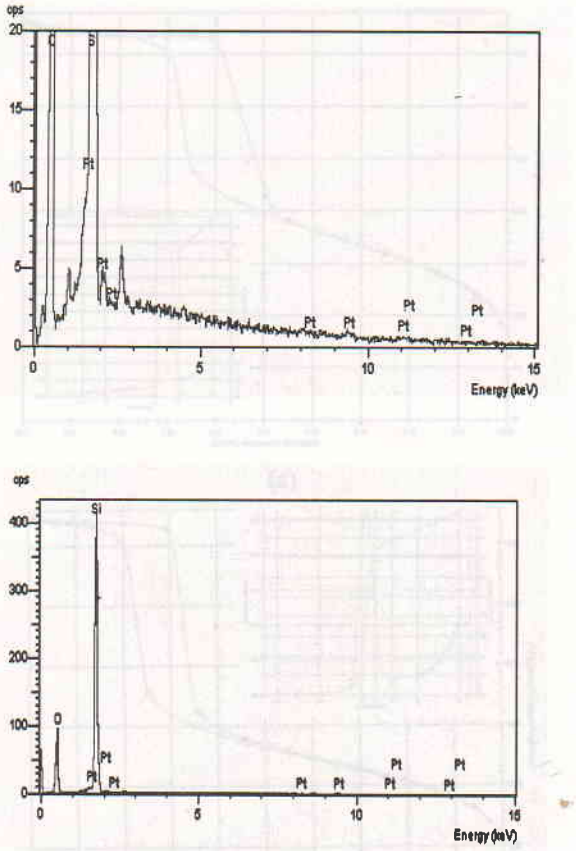
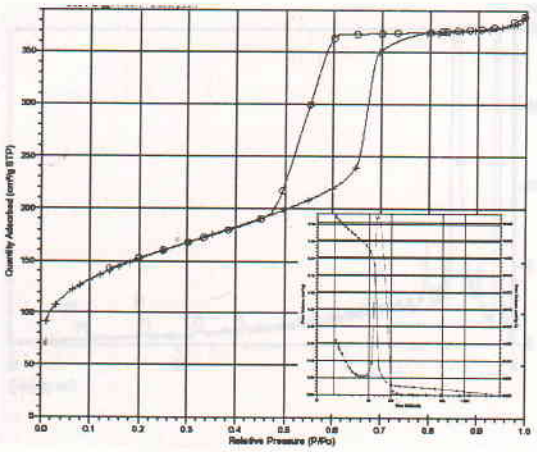


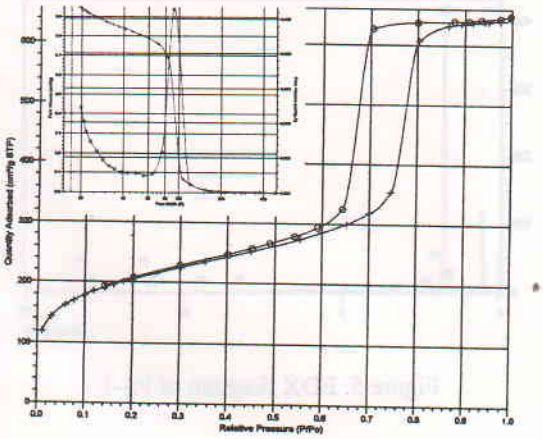
Figure 5. EDX diagram of PS-1.

d. N_2 adsorption-desorption method

All N_2 adsorption-desorption isotherms are type IV with a H1 hysteresis loops according to IUPAC classification, indicating that there exist mesopore in all samples with cylindrical pore structure. The BJH pore size distribution curves are very sharp indicating the very regular pore diameter of these materials. Capilary condensation of SBA-15 begins at P/P_o=0.6 higher than 1%Pt/SBA-15 (P/P_o=0.5) and the wide of hysteresis loop of SBA-15 larger than PS-1 show that after supporting plantinum on SBA-15 material, the pore size of this denatured material decreases.



(a)



(b)

Figure 6. Nitrogen adsorption isotherms measured at -196°C and the corresponding BJH pore size distribution of SBA-15 (a) and 1% Pt/SBA-15 (b) samples.

All parameters about surface area, pore diameter, pore volume,... of these materials are showed in table 1:

Table 1. Physical parameters of SBA-15 and PS-1 mateials

Samples	S_{BET} (m^2/g)	V_t(cm^3/g)	D_p (nm)
SBA-15	727	1,08	6,77
1%Pt/SBA-15	342	0,49	5,83

The results in table one show the average pore diameter, pore volume and BET surface area decrease obviously with an incorporation of Pt into SBA-15 material and this proves that platinum with very small nano sizes was dispersed inside the pore of support material.

3.3. Catalytic activities of Pt/SBA-15 in the oxidation of D-glucose

The results of the oxidation of D-glucose carried out on Pt/SBA-15 catalyst were presented in table 2:

Table 2. The results of the oxidation of D-glucose over different catalysts
(Temperature: 80°C; Air flow rate: 20ml/min; Time: 2 hours)

Catalysts	Conversion of glucose (%)	Composition of products (%)			
		Gluconic acid	Lactone	Disaccharide	Other products
HNO_3	87,67	15.80	15,69	12,60	57,01
PS-1 (pH~9)	74,54	86,63	3,16	8.20	2,01
PS-2 (pH~9)	70,14	85,81	3,64	8,57	1,98
PS-3 (pH~9)	48,87	86,56	3,25	8,11	2,08
PS-1 (pH^*)	51,72	53,04	22,73	22,42	1,81

- Other products: Tartaric, threonic, acrylic acids, and the products of decarboxylation ...

- pH^*: The oxidation reaction was performed without pH control

- From the results above, we found that both HNO_3 and Pt/SBA-15 present a good conversion in the oxidation reaction of glucose. The conversion of the reaction reached 87.67% when using HNO_3 as oxidizing agent, but the selectivity of D-gluconic product is quite low. The high oxidation ability with high acidity of HNO_3 make the reaction occur at many positions and in different ways, so by-products occupy at very high level (~84%).

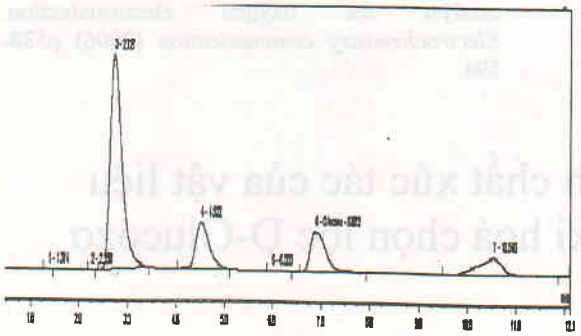


Figure 7. HPLC-RID image of the products of D-glucose oxidation on PS-1 catalyst

On the other hand, the reaction on Pt/SBA-15 catalysts with pH control not only showed a high conversion, but also high D-gluconic acid selectivity. This determined a good suitability of plantinum nanoparticles in the selective oxidation of glucose. When the reaction was performed without pH control on PS-1 catalyst, the conversion decreased significantly. The pH at the end of the reaction was about 2.7. This condition facilitated the formation of gluconolactone and disaccharide and inhibited the catalyst activity [2]. So, we should add alkaline solution continuously to maintain pH value at 9 during the oxidation process. In table 2, we also see that increasing the Pt contents led to decrease in catalytic activity. The average particle size of the catalyst with the lower platinum content (1%) is smaller (<6nm) than that of the catalyst with 2 and 3% Pt contents, which has an average particle size of 10-15 nm (TEM images) explained for this difference. On the other hand, Pt nanoparticles existed inside the pore channels of SBA-15 (PS-1), active sites are located in confined spaces, so the collision rate of these sites with glucose molecules increase and catalytic activity of nanoparticles inside will be better than large clusters outside the pore channels of support material.

4. Conclusions

In conclusion, SBA-15 was successfully prepared by hydrothermal synthesis using Pluronic P123 as template and TEOS as silica source. The synthesized material has high specific surface area, narrow pore size distribulation, and large pore with high wall thickness which is very suitable for using as support material. Platinum was dispersed effectively on SBA-15 by incipient wetness method and still kept the original 2D hexagonal mesostructure. When Pt loading is about 1% by mass, Pt nanoparticles were highly dispersed with the size under 6nm in the channels of SBA-15 and at this state, Pt/SBA-15 catalyst showed the highest activity and selectivity in the oxidation of glucose. When increasing the content of Pt loading, most Pt nanoparticles aggregated outside the channels of SBA-15 with size of 10-15nm and catalytic activities of these materials decreased. pH value also affects directly on the selectivity of gluconic acid product and the best condition for the reaction is pH 9.

Acknowledgement

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Nghiên cứu đặc trưng và tính chất xúc tác của vật liệu Pt/SBA-15 trong phản ứng oxi hoá chọn lọc D-Glucozơ

Trần Thị Như Mai, Nguyễn Thị Minh Thư, Phạm Đình Trọng, Nguyễn Thị Hà, Giang Thị Phương Ly

Khoa Hóa học, Trường Đại học Khoa học Tự nhiên, ĐHQGHN, 19 Lê Thánh Tông, Hà Nội

Trong bài báo này, Pt nano được phân tán lên vật liệu mao quản trung bình SBA-15 bằng phương pháp tẩm dung dich rồi kết tủa bằng chất khử $NaBH_4$.. Các mẫu vật liệu tổng hợp được đặc trưng bằng các phương pháp XRD, TEM, EDX, Hấp phụ và giải hấp phụ N_2.

Vật liệu SBA-15 tổng hợp được có mao quản hexagonal 2D có độ trật tự cao. Pt đạt kích thước nano phân tán trong mao quản và ngoài mao quản phụ thuộc vào nồng độ tiền chất và điều kiện phân tán. Hoạt tính xúc tác được đánh giá trong phản ứng oxi hoá glucozơ. Phản ứng được thực hiện ở pha lỏng, nhiệt độ 80oC, tốc độ thổ khí 20 ml/phút và ở pH 9. Xúc tác chứa Pt nano có hiệu quả tương đối cao cho quá trình oxi hoá chọn lọc glucozơ tạo axit gluconic.Từ kết quả phân tích sản phẩm phản ứng bằng HPLC-RID cho thấy hàm lượng, kích thước hạt xúc tácPt ảnh hưởng đến độ chuyển hoá glucozơ trong khi pH có ảnh hưởng quyết định đến tính chọn lọc axit gluconic và các phản ứng phụ. Xúc tác 1% Pt/SBA-15 cho độ chọn lọc axit gluconic cao.