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Review

Synthesis of sodium gluconate by bismuth promoted Pd/C catalyst

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Bi promoted Pd/C catalyst (Bi-Pd/C) was prepared and evaluated for glucose oxidation. Reaction rate depends on Bi and Pd ratio on activiated carbon. Best promotion effect was got when $PdCl_2$ to $Bi(NO)_3$•5H2O weight ratio was 1 to 3 during catalyst preparation. Compared with other noble metal catalyst, the reaction time was shortened and Bi prevented Pd/C deactiviation during this reaction. The reaction cycles for this catalyst was increased compared to Pd/C catalyst alone. Through XPS analyzation, Bi and Pd was observed to be formed on the surface of activiated carbon particles. This catalyst can be used for industrial process to oxidize glucose to sodium gluconate.

Key words: Glucose oxidation, synthesis, sodium gluconate, Bi-Pd/C catalyst.

INTRODUCTION

The outstanding property of sodium gluconate is its excellent chelating power, especially in alkaline and concentrated alkaline solutions. It forms stable chelates with calcium, iron, copper, aluminium and other heavy metals, and in this respect, it surpasses all other chelating agents, such as EDTA, NTA and related compounds.

Aqueous solutions of sodium gluconate are resistant to oxidation and reduction, even at high temperatures. However, it is easily degraded biologically, and thus presents no waste problem. In ready mixed concrete industry, it is used as setting retarder. It is also used in detergent industry, bottle and dish washing, cleaning of machinery, equipment and transport cages used in food processing, cleaning agent for ceramic surface, etc.

Sodium gluconate is manufactured by fermentation process in large commercial scale. For fermentation process, it produces waste water and environment problem. In recent years, catalystic process is more preferred. For noble metal catalyst process, which is a green chemical process, catalyst deactiviation and short lifetime of catalyst also cause problems for production. A lot of research work has been done to improve effectiveness of catalyst and prevent catalyst deactivation by promoter such as lead, bismuth, etc. Lead and bismuth are the most common promoters but many others including Cd, Tl, Ag, Te, Se, Co, Ce and Sn have been proposed (Michele, 2003; Mirelle et al., 2002). When used alone, these elements are inactive for the concerned oxidation reactions, but when associated with the noble metal, they considerably increased the overall catalytic performances (activity, sometimes selectivity) and/or the lifetime of the catalysts (Mirelle et al., 2002).

In our research program, our aim is to produce sodium gluconate in large scale. Therefore, the economical and practical consideration is a very important factor. The bismuth promoted Pd catalyst is our first selection for our research. The total cycles or lifetime, activity, selectivity and recycle of noble metals are very important factor in industrial production.

Experiments

Ground and activiated charcoal (average diameter of 6 μm) was provided by Nanjing Forest University. Palladium chloride, bismuth nitrate, glucose and other reagents were manufactured by Shanghai Reagent Company.

Catalyst preparation

A solution of 1.7 g of palladium chloride in 1.7 ml of concentrated hydrochloric acid and 20 ml of water was prepared by heating on a water bath for 2 h or until solution is complete. It was then added to a solution of 30

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g of sodium acetate trihydrate in 200 ml of water contained in a 500 ml hydrogenation flask. 20 g of ground activated charcoal and hydrogenate was added in an atmospheric hydrogenation apparatus until absorption ceases. The catalyst was collected in a bucher funnel, washed with five 100 ml portions of water and sucked as dry as possible. The catalyst was dried at room temperature over potassium hydroxide pellets or anhydrous calcium chloride in vacuum desiccators. The powdered catalyst (approx 20 g yield) was stored in a tightly stoppered glass bottle. 5.1 g of bismuth nitrate was dissoved in 30 ml water and 2 ml concentrated hydrogen hydrochloric acid. The prepared catalyst was added into the bismuth nitrate solution. 6 ml 37% formaldehyde solution was added in this mixture and the pH adjusted to 10, and further mixed it for 20 min. The catalyst was filtrated and washed by distilled water 5 times.

Evaluation of catalysts

Reference catalyst 5% Pd/C, 5%Pt/C and 1%Pt 5%Pd/C were provided by Johnson Mathey. Catalyst 5% Pd/C and 5%Bi 10%Pd were prepared as mentioned above in our laboratory. The oxidation of glucose solution was performed in a thermostated glass reactor of 500 ml equipped with a stirrer, an air supply system, a burette containing 4 N NaOH and a pH electrode. The acids formed during the oxidation of glucose were neutralized by addition of aqueous solution of sodium hydroxide to maintain constant pH at 9.0 in the reaction medium.

Standard oxidation procedure

The glucose solution (50 g glucose monohydrate in 250 ml distilled water) was heated in the reactor to 50°C. Once the temperature was stabilized, the catalyst was added to the solution and oxidation reaction started by introducing air (flow rate 0.5l/s) in the stirred slurry. The mixture is stirred at 1200 rpm. After total required amount of base was added, the catalyst was removed from the reaction mixture by filtration. The catalyst was washed by distilled water for next run.

Catalyst characterization techniques

XPS was performed on an SSI-X-probe spectrometer form Fisons, using the Al Kα radiation (E=1486.6eV). The energy scale was calibrated by taking the Au 4f7/2 binding energy at 84 eV. The C1s binding energy of contamination carbon set at 284.8 eV. The analyses of bismuth and palladium were based on Bi 4f 7/2and Pd 3d5/2 photopeaks.

RESULTS AND DISCUSSIONS

Different catalysts and reaction rates

Different noble catalysts had different reactivity for glucose oxidation as consumption rate of sodium hydroxide

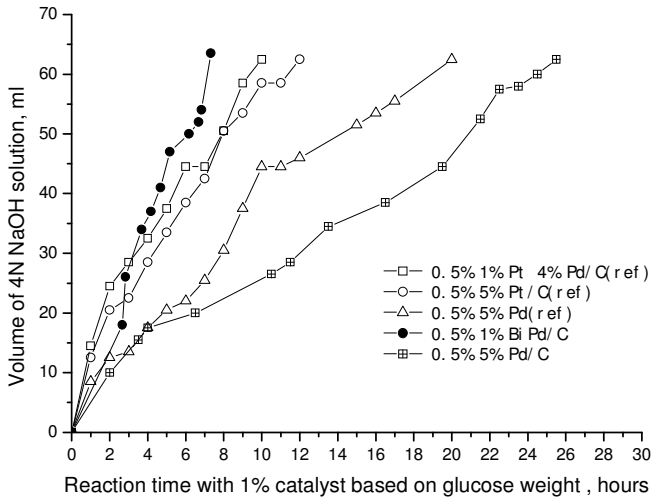

Figure 1. Different catalyst and reaction rate for glucose oxidation.

is proportional to the reaction rate. The results are displayed in Figure 1 as the first cycle of catalysts reaction. The catalysts usage is kept the same for 0.5% weight of glucose in each run. Monometallic noble catalysts such as Pd/C (ref), Pt/C (ref) and Pd/C are slower than bimetal Bi-Pd/C catalyst. Bi is a very effective promoter for Pd/C catalyst, the reaction rate is fastest and overall reaction time is the shortest in all selected catalyst. In the absence of bismuth, the activity and selectivity of palladium in glucose oxidation are much lower because of catalysts deactivate. This is attribute to oxygen poisoning of the metal surface which is particle size dependent because palladium particles smaller than 2 nm have a high affinity for oxygen (Michele et al., 1995). On the other hand, Pt had very little effect to promote this oxidation reaction on Pd/C catalyst.

Catalyst dosage and reaction rate

For the Bi-Pd catalyst, the reaction rate was related to the catalyst amount at 0.25, 0.5 and 1.0% based on glucose monohydrate. The reaction rate is proportional to the amount of catalyst used for this oxidation reaction as illustrated in Figures 2 and 3. Compared with the other researcher's data (Michele et al., 1995), (glucose) / [Pd] =787, the reaction time was 2.5 h, for our catalyst Bi Pd /C catalyst, at 1% dosage of glucose, (glucose / [Pd] = 1666, the reaction duration is about 4 h.

So the catalyst reactivity is quite fast and reasonable for possible industrial application.

Lifetime and cycles for Bi-Pd catalyst

Bi-Pd/C catalyst was used in 11 and 21 successive oxidation with catalyst usage of 0.5 and 1.0%. Reaction rate was slower as reaction cycles increased as showed in Figure 4. It is well known that noble catalyst is deacti-

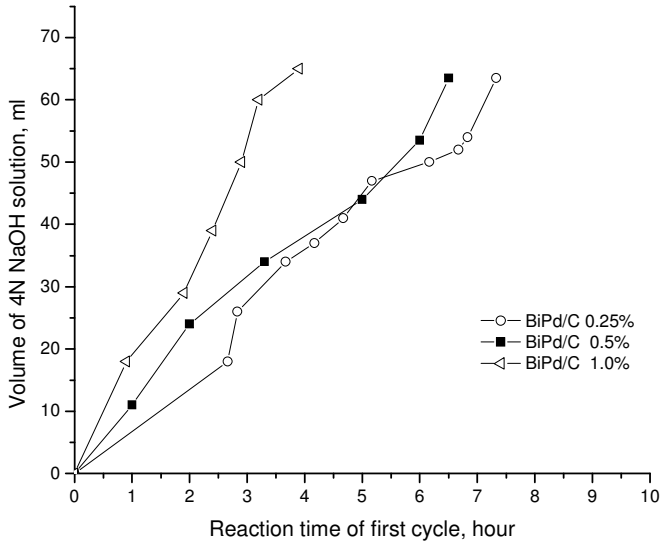

Figure 2. Correlation between catalyst amount and reaction rate.

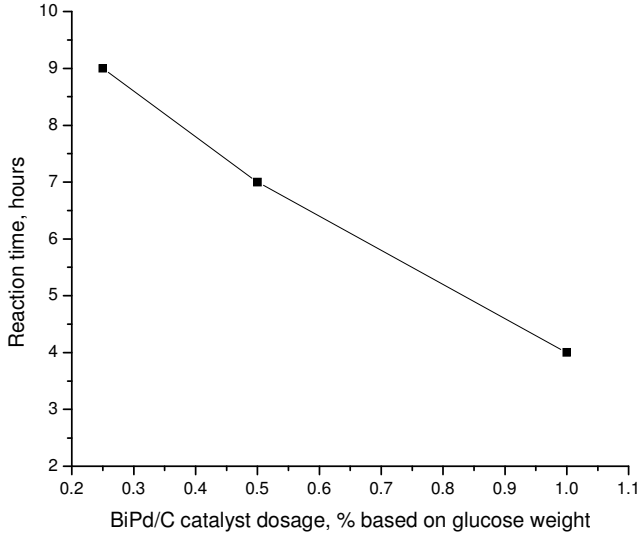

Figure 3. Correlation between catalyst dosage and total reaction time.

viated during glucose oxidation. Bi can be dissolved in reaction solution because of great chelating power of sodium gluconate. During our research, for every reaction cycle, a very small amount of catalyst adsorbed on polymer filter for separation of catalyst. This is also a reason for slower reaction rate for Figure 4. As reported by other researchers, bismuth is dissolved in reaction mixture and leached in every reaction cycles. For dosage of 1.0% Bi-Pd catalyst, the remaining Bi atoms on catalyst are very small, and catalyst is deactiviated by loss of Bi. Deactivation studies are made difficult because of the high number of factors potentially involved: sintering or leaching of active components, poisoning of active sites by heteroatom-containing molecules, inactive metal

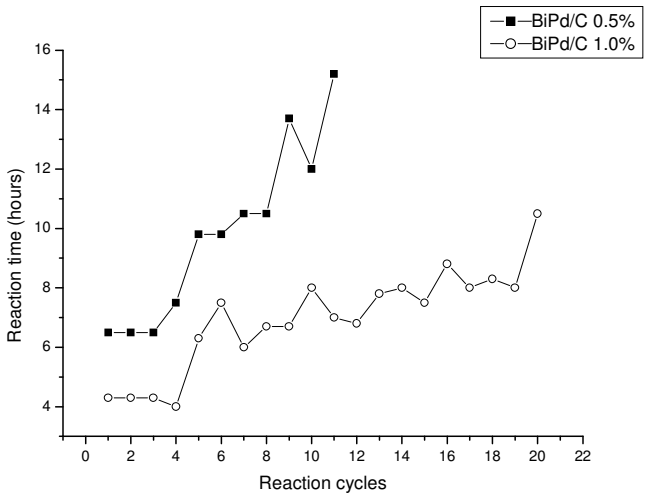

Figure 4. Correlation between reaction rate and reaction cycles.

or metal oxide deposition, impurities in solvents and reagents, and oligomeric or polymeric by-products (Michele, 2003). The kinetic aspects of glucose oxidation can be treated in two extreme regimes: intrinsic kinetic regimes (Kluytmans, 2000), i.e. the reaction rate is determined by the chemistry at the catalytic site and not limited by mass transfer and diffusion effects, and the second is full oxygen mass transfer and diffusion. When the reaction of the catalyst is diminished or the catalyst becomes partly deactivated, an unpromoted Pd/C catalyst falls on first regime, while Bi promoted Pd/C catalyst falls in the second category.

XPS analyzing

Fresh Bi-Pd/C catalyst was analyzed by XPS. Table 1 showed that the elements present in the catalyst were Pd, Bi, and C. The binding energy for Pd metal is 335.70 eV and PdO is 337 eV. The binding energy for Bi is around 162.60 eV, indication of oxide species Bi_2O_3 (159.1 eV), not the metal (156eV) as eV taken form a XPS database (http://www.lasurface.com/Data_base). Overall, Bi is in the form of oxide and Pd is in metal and oxide species on the catalyst surfaces.

Conclusions

Bi-Pd/C catalyst is a very promising catalytic material for industrial production of sodium gluconate with the advantage of simple and green chemical process compared with enzymatic process. For industrial applications, noble metal catalyst should be repeatedly used in continuous mode for long time. The lifetime of present BiPd/C is very long with more than 20 cycles. In addition, these processes offer the important advantages of high simplicity of operation and they are environmentally friendly since almost no effluents are generated. Bi promotion of Pd/C catalyst is very effective and finally finds a solution to

Table 1. XPS characterization of BiPd/C catalyst.

Peak ID	At %	Center (eV)	FWHM	Area	Normal	S.F	Stoic
C_{1s}	97.62	284.75	1.40	10407	41628	0.25	1.000
Pd_{3d}	1.33	335.70	6.60	2608	4.60	4.60	0.014
Bi_{4f}	1.05	162.60	9.10	3320	7.40	7.40	0.011

Pd/C deactiviation during glucose oxidation. The best Bi promotion is obtained when $PdCl_2$ to $Bi(NO)_3.5H_2O$ weight ratio is 1 to 3 for catalyst preparation. The exact mechanism is not very clear, but this promotion is very useful for industrial large scale production for sodium gluconate. Further research work is needed to be done to make better use of the used catalyst or reactiviate the used Bi-Pd/C catalyst. Other possible research is the re-absorption of Bi to used catalyst to lengthen the lifetime of used catalyst.

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