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PAPER

Aerobic oxidation of 5-hydroxymethylfurfural (HMF) effectively catalyzed by $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ supported Pt catalyst at room temperature

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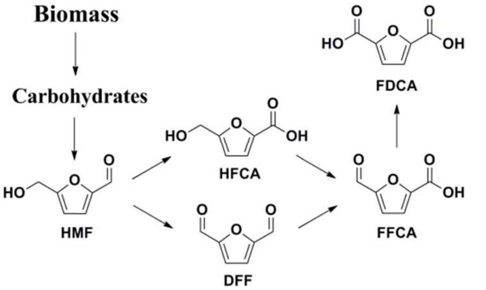
It efficiently catalyzed the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) when Pt nanoparticles (NPs) were supported on $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ solid solution. 98% yield of FDCA was achieved within 30 min at room temperature and the catalyst was well reused for five times without much loss of the FDCA selectivity. It is the first report about the oxidation of HMF, an alcohol and an aldehyde, effectively catalyzed by a ceria-based material supported Pt catalyst. The natural properties of the Pt NPs and the ceria-based support were retained and not affected after their combination. The superior oxygen activation ability of the Bi-doped ceria changed the performance of the ceria supported Pt catalyst thoroughly. Pt NPs were responsible for the formation of the Pt-alkoxide intermediate and then the β-H elimination with the help of the hydroxide ions. Bi-contained ceria accelerated the oxygen reduction process because of the presence of large amount of oxygen vacancies and the cleavage of peroxide intermediate promoted by bismuth. These specific functions were well incorporated during the catalytic oxidation cycle, leading to the generation of the highly efficient $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst for HMF oxidation at room temperature.

Introduction

That using the abundant biomass resources to replace petrochemicals is an urgent demand for sustainable chemistry.[1-3] 5-Hydroxymethylfurfural (HMF), a key biomass-derived platform chemical that can be obtained by dehydration of carbohydrates in acidic media, has a high potential as a versatile chemical intermediate.[4] The focus on the selective oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) has increased notably in recent years. FDCA is a possible alternative to substitute fossil-based terephthalic, isophthalic and adipic acids for polymers preparing. It is also a promising chemical intermediate for the preparation of fine chemicals, pharmaceuticals and others.[5-7] Considering these estimable applications, FDCA was listed as one of the top twelve value added chemicals from biomass by the US department of energy in 2004.[2]



Scheme 1 The oxidation of biomass-derived HMF to FDCA

The oxidation of HMF to FDCA comprises an alcohol oxidation and an aldehyde oxidation (Scheme 1).[8, 9] In most catalytic systems, the aldehyde side chain of HMF was easily oxidized and 5-hydroxymethyl-2-furancarboxylic acid (HFCA) was obtained at the initial reaction stage. The following oxidation of the alcohol group to aldehyde and thus the production of 5-formyl-2-furancarboxylic acid (FFCA) was the rate-limiting step.[9-12] The oxidation of alcohols is also a pivotal reaction in organic chemistry, affording versatile carbonyl compounds. Using molecular oxygen instead of stoichiometric inorganic oxidants as terminal oxidant is a preferable alternative for both economic and environmental benefits.[13-16] Though various catalysts have been applied successfully in HMF oxidation to FDCA, long reaction time, high temperature and high molar ratio of the precious metal to HMF were often demanded to obtain a high FDCA yield. It remains a major task to develop efficient catalysts for HMF oxidation using molecular oxygen as terminal oxidant in eco-friendly aqueous medium and at moderate reaction conditions.

For a redox reaction including the electron gain or loss, reducible oxide was a suitable selection as the catalyst or the catalyst carrier.[17-19] Ceria-based substance containing the Ce^{IV}/Ce^{III} redox couple and oxygen vacancies was a promising catalytic material and has drawn much attention in the field of catalytic oxidation.[19-21] In our previous work, $Ce_{1-x}Bi_xO_{2-\delta}$ ($0.08 \le x \le 0.5$) were found to catalyze HMF to HFCA and 2,5-bishydroxymethylfuran (BHMF) in the presence of oxygen in alkaline aqueous solution. While as excellent support for Au nanoparticles (NPs), $Ce_{1-x}Bi_xO_{2-\delta}$ ($0.08 \le x \le 0.2$) catalyzed HMF oxidation to FDCA.[22] Despite the Bi-doped ceria which existed alone was inactive towards catalyzing the conversion of the alcohol group in HMF, the oxygen activation and hydride transfer were enhanced by the presence of the large amount of oxygen vacancies and the specific Bi during the catalytic cycle. The Bi-doped ceria should also be a superior support for other components which could afford the active sites for the activation of the C-H bond in the alcohol group, resulting in the generation of active catalysts for HMF oxidation.

The performances of the Au and Pt catalysts towards HMF oxidation at conditions of 295 K, 690 kPa O_2, 0.15 M HMF and 0.3 M NaOH have been compared previously.[8] Though the activity of the Au catalysts was much higher than that of the Pt catalysts, the Pt catalysts showed better selectivity to FDCA. The initial turnover frequency of HMF conversion was an order of magnitude greater on Au catalysts compared to Pt. However, the major product with the Au catalysts was HFCA. While longer time was needed for Pt catalyst to achieve the complete conversion of HMF, the desired diacid product was obtained in majority. The results implied that the dehydrogenation of the alcohol group and thus the achievement of the final production of FDCA were energetically more favorable with a Pt catalyst, which had also been shown for other alcohols oxidation.[13, 23] In addition, the stability of Au catalysts limited its industrial application.[9, 22] In this work, Pt NPs were combined with the $Ce_{1-x}Bi_xO_{2-\delta}$ support for catalyzing HMF oxidation to FDCA. Gratifyingly, Pt/CeO_2 showed poor catalytic activity just as a previous report,[24] while $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst showed excellent performance at room temperature. Unlike ceria supported Au catalyst, the Pt NPs and the ceria-based support remained their natural properties after combination, the excellent catalytic oxidation activity of the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst was derived from a well incorporation of their specific functions. To the best of our knowledge, it is the first report about HMF, a kind of alcohol and aldehyde, oxidation efficiently catalyzed by a ceria-based material supported Pt catalyst.

Experimental

Chemicals and characterization

All the chemicals were used without further purification. HMF (98%) and BHMF (98%) were obtained from InnoChem Science & Technology Co. Ltd (Beijing). FDCA (97%), HFCA and FFCA (98%) were purchased from J & K Co. Ltd (Beijing). Polyvinylpyrrolidone (PVP), $Bi(NO_3)_3{\cdot}5H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were obtained from Aladdin Chemicals Co. Ltd (Shanghai). Concentrated H_2SO_4, concentrated HNO_3, NaOH, citric acid monohydrate and ethylene glycol were obtained from Beijing Chemicals Co. Ltd (Beijing). $H_2PtCl_6{\cdot}6H_2O$ was achieved from Shanghai Shi Wu Chemical Reagent Science and Technology Co. Ltd (Shanghai).

The powder X-ray diffraction (XRD) patterns were carried out on a Bruker D8 Advance X-ray diffractometer using a Cu Kα radiation source (λ = 1.5406 Å). The powder samples were placed on a glass slide and scanned from 20° to 80° at a rate of 10°/min or 1°/min.

Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. The powder was ultrasonically dispersed in ethanol and the suspension was deposited on a copper grid coated with a porous carbon film.

Elemental contents were measured by ICP-OES (iCAP 6300 Thermo Scientific USA). Typically, a sample with an amount of 0.1 g was subjected to microwave assisted digestion with 6 mL HCl and 2 mL HNO_3 at 200 °C for 1 h, then diluted by deionized water and analyzed along with known solutions.

Catalyst preparation

Porous $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0, 0.1, 0.2, 0.5) samples were prepared by the citrate method and the specific process was described in our previous report.[22]

Pt was loaded onto $Ce_{1-x}Bi_xO_{2-\delta}$via the sol-impregnation method. For the preparation of Pt NPs stabilized by PVP,[25] 0.72 g PVP (K30) was dissolved in 27.05 mL of 0.024 M H_2PtCl_6 aqueous solution and the solution was mixed with 243.5 ml ethylene glycol. Then, the reaction mixture was refluxed at 200 °C for 1.5 h. Within minutes, the color of the solution changed from orange to dark brown, showing the formation of Pt NPs. The as-synthesized colloid were purified and collected by adding a large excess of acetone (nearly triple volume) and stirring overnight. After discarding the supernatant, the flocculated Pt NPs were re-dispersed in a specified volume of ethanol. Pt sol of perfectly known concentration was obtained. 1 wt% Pt NPs on $Ce_{1-x}Bi_xO_{2-\delta}$ was prepared by wet impregnation of $Ce_{1-x}Bi_xO_{2-\delta}$ with Pt sol. The suspension was evaporated by heating at 70 °C and then dried at 70 °C overnight without further treatment. The loading amount of Pt was verified by ICP-OES analysis.

HMF oxidation

The aqueous phase catalytic oxidation of HMF was performed in a 50 ml autoclave equipped with a PTFE liner and a magnetic stirrer. In a typical process, 6 ml of 0.15 M HMF and 0.6 M NaOH solution was added to the reactor along with appropriate amount of catalyst. The autoclave was flushed with O_2 3 times and pressurized at 1.0 MPa. After reacting for a certain time at room temperature under stirring, the sample was centrifuged, acidified with sulfuric acid and diluted with water. The resulting solution was filtered using a syringe filter (0.2 μm) before analysis in a high performance liquid chromatograph (HPLC) equipped with a Waters 2487 Dual λ absorbance detector. The HPLC utilized a Bio-Rad Aminex HPX-87H column at 35 °C and 5 mM H_2SO_4 flowing at 0.5 $ml{\cdot}min^{-1}$ to perform the separation. The identification and quantification of HMF, HFCA, FFCA, DFF and FDCA were carried out by injecting known concentrations. The yield of BHMF was determined by gas chromatography (GC) analysis.

Results and discussion

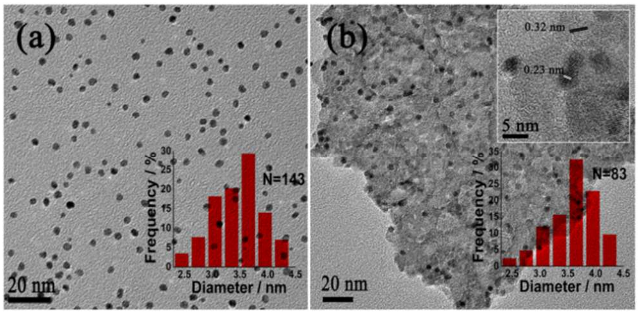


Fig. 1 TEM images and Pt particle size distributions of (a) PVP stabilized Pt sol and (b) Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ (inset of b: HRTEM of Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$). N indicated the number of particles included in each particle size distribution.

Monodisperse Pt NPs with a narrow size distribution of (3.5 ± 1) nm (Fig. 1a) were prepared following the ethylene glycol reduction method under the protection of PVP. The Pt NPs were well dispersed and remained nearly unchanged after supporting on the $Ce_{1-x}Bi_xO_{2-\delta}$ samples via the conventional wet impregnation method (Fig. 1b). Two lattice fringes of 0.23 nm and 0.32 nm ascribed to the d spacing values of the {111} planes of Pt and Bi-doped ceria could be seen from the HRTEM result of the Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ sample (inset of Fig. 1b).[26] The proportion of the larger particles that were more than 3.5 nm was increased, which was perhaps caused by the interaction between the Pt NPs and the support or some of the small Pt particles in the pores of the support.

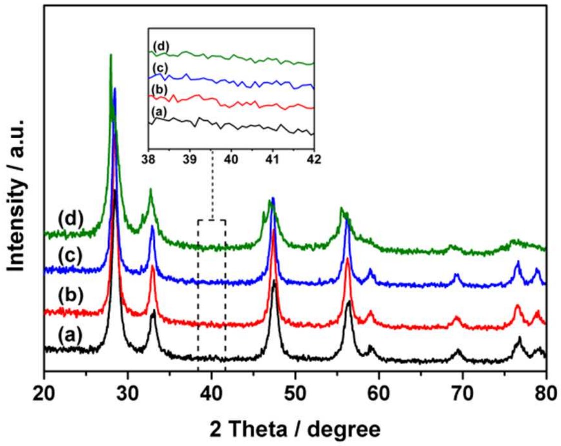


Fig. 2 XRD patterns of (a) Pt/CeO_2, (b) Pt/$Ce_{0.9}Bi_{0.1}O_{2-\delta}$, (c) Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and (d) Pt/$Ce_{0.5}Bi_{0.5}O_{2-\delta}$ samples (inset: XRD of samples scanned at low speed).

XRD patterns of the four Pt/$Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0, 0.1, 0.2, 0.5) samples were also taken and the results are shown in Fig. 2. Only peaks ascribed to the supports were found. The absence of the diffraction line for the Pt phase, such as the strongest diffraction peak at 39.75° (inset of Fig. 2), also indicated that platinum was highly dispersed throughout all the supports.

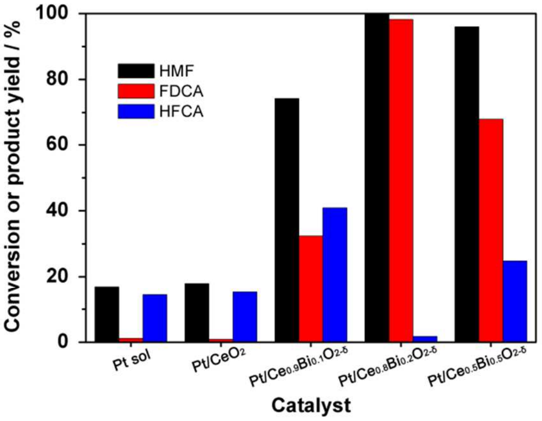


Fig. 3 HMF conversion, FDCA and HFCA yields on different studied catalysts (Pt : HMF = 5×10^{-3} mol/mol, 4 equiv. NaOH, 1.0 MPa O_2, 23 °C, 30 min).

HMF oxidation was then carried out with the Pt sol or the obtained Pt/$Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0, 0.1, 0.2, 0.5) samples at room temperature. The results are shown in Fig. 3. The Pt sol alone presented as catalyst in the reaction system displayed poor activity towards HMF oxidation to FDCA. Only 17% conversion of HMF with 1% and 15% yields of FDCA and HFCA were obtained after reaction for 30 min. It indicated that the Pt sol was merely a little active for the oxidation of the aldehyde group but inactive for the oxidation of the alcohol group in HMF at these moderate reaction conditions. The Pt/CeO_2 showed a similar catalytic performance with the Pt sol, implying that the CeO_2 was an inactive support for Pt NPs. It was identical with a previous report.[24] That the CeO_2 support did not influence the performance of the Pt sol was also found. All the Bi-contained catalysts showed preferable catalytic activities compared to the Pt sol and the Pt/CeO_2 catalyst, especially the Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ which afforded a 100% conversion of HMF and a 98% yield of FDCA at the same conditions. The catalytic performance of all these catalysts followed the order: Pt sol ≈ Pt/CeO_2 << Pt/$Ce_{0.9}Bi_{0.1}O_{2-\delta}$ < Pt/$Ce_{0.5}Bi_{0.5}O_{2-\delta}$ < Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$. A control experiment without catalyst was also carried out under the same conditions. Nearly 10% conversion of HMF was obtained and the major products were derived from the degradation of HMF. To achieve a high yield of FDCA, active catalyst was needed to convert HMF quickly at the beginning of the reaction period, thus inhibiting the degradation of HMF and keeping a high selectivity to the desired oxidation products.

The catalytic oxidation of HMF to FDCA in water using PVP stabilized Pt NPs as catalyst has previously been investigated by Siankevich et al., 100% conversion of HMF and 95% yield of FDCA were obtained with molecular oxygen as oxidant.[27] However, a high catalyst loading of 5 mol% and a long reaction time of 24 h were needed even the reaction was conducted at 80 °C. The results above emphasized the importance of combining noble metal NPs with active support for the preparation of highly effective catalyst. In addition, the Pt NPs catalyst could be recovered easily by filtration or centrifuging after supporting on bulk material.

The fact that the catalytic activity was nearly unchanged when Pt sol was deposited on CeO_2 while increased sharply when deposited on $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1, 0.2, 0.5) samples was to some degree identical with our previous work. In the previous work, $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1, 0.2, 0.5) exhibited excellent catalytic performance on converting HMF to HFCA and BHMF in alkaline aqueous solution without degradation of HMF, while CeO_2 was inactive for the reaction and led to the serious degradation of HMF at the same conditions.[22] Then, the $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1, 0.2, 0.5) catalysts were further examined for the conversion of HMF at room temperature to identify the difference of their catalytic activities.

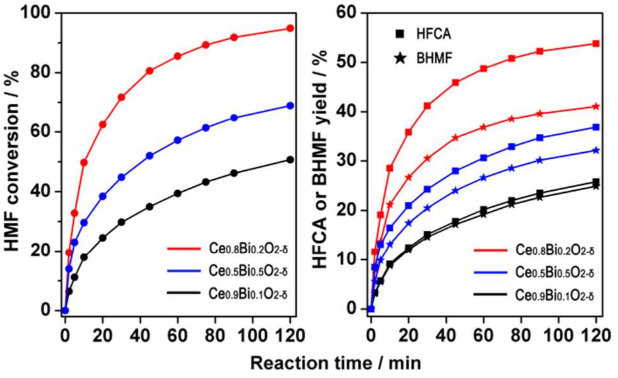


Fig. 4 HMF conversion and product yields as a function of reaction time during HMF reaction in aqueous solution over $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1, 0.2, 0.5) catalysts (0.1 g catalyst, 4 equiv. NaOH, 1.0 MPa O_2, 23 °C).

As shown in Fig. 4, HMF was efficiently converted to HFCA and BHMF with the presence of all the three Bi-doped ceria catalysts. The catalytic activity followed an order of $Ce_{0.9}Bi_{0.1}O_{2-\delta}$ < $Ce_{0.5}Bi_{0.5}O_{2-\delta}$ < $Ce_{0.8}Bi_{0.2}O_{2-\delta}$, which was in the exact same sequence with $Pt/Ce_{1-x}Bi_xO_{2-\delta}$ catalyzing HMF oxidation at the same conditions (Fig. 3). This result indicated that the natural difference among the three $Ce_{1-x}Bi_xO_{2-\delta}$ supports was remained after supporting Pt NPs and the Pt NPs did not influence the ceria-based support playing its own role during the catalytic oxidation cycle. For the conversion of HMF to HFCA and BHMF catalyzed by Bi-doped CeO_2, BHMF and HFCA were obtained equally from the Cannizzaro reaction of HMF and HFCA was also product from the oxidation of the aldehyde group in HMF. The differences between the yields of HFCA and BHMF (Fig. 4) implied that the catalytic oxidation activity of the Bi-doped ceria also followed the same order. It was identical with previous works in which doping 20 mol% of bismuth in ceria showed the best performance towards oxidation reaction or oxygen storage.[28, 29]

As analyzed above, the inactive CeO_2 support did not change the catalytic oxidation activity of the Pt sol (Fig. 3) after their combination. The active Bi-doped ceria samples showed preferable activities after depositing Pt NPs and the discrimination between them were retained at the same time. It urged us to know that the Pt NPs and the ceria-based support did not influence their mutual functions when coexisting in the reaction system. The exclusive roles of the Pt NPs and the Bi-doped ceria were synergistic well during the catalytic oxidation cycle.

Under the same conditions as Fig. 3 except for the presence of base, reaction resulted in very low conversion of HMF with the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst. Only DFF, with nearly negligible amount, was detected besides HMF in the solution after reaction. It indicated that base played an essential role during the reaction process and this result was identical with previous reports.[30-32] Zope et al.[30] investigated the reaction mechanism of ethanol and glycerol selective oxidation to acids over supported metal catalysts in aqueous phase by using density functional theory calculations and labeling experiments with $^{18}O_2$ and $H_2{}^{18}O$. They suggested that the cleavage of the O-H and C-H bond in alcohols and thus the production of aldehyde were generally facilitated by the noble metal catalyst and the hydroxide ions which presented in the solution or as the surface bound hydroxide intermediates. Oxygen atoms incorporated into the acids products were originated from hydroxide ions instead of molecular oxygen. Molecular oxygen participated in the catalytic cycle by removing the electrons depositing into the metal particles. This O_2 reduction process regenerated hydroxide ions via the formation and dissociation of peroxide intermediates. Moreover, the mechanism above was also found suitable for the selective oxidation of HMF to FDCA.[32]

The Pt NPs in all the $Pt/Ce_{1-x}Bi_xO_{2-\delta}$ catalysts were the same and the reaction conditions, including the alkali concentration were identical (Fig .3). The dramatic difference among the catalysts should be rooted in the oxygen activation ability of the supports. Theoretical studies by Teng et al.[19] showed that CeO_2 could serve as an electronic repository, gain and store electrons from the supported metal cluster and release them when the metal particle interacted with molecular O_2. This function was related to the reducible property of CeO_2. The incorporation of Bi_2O_3 into CeO_2 lattice changed its dynamic redox activity at low temperature drastically.[28] We can reasonably deduce that the Bi-doped ceria captured the electrons from the Pt NPs more easily during the O-H and C-H bond activation processes. The Pt NPs was recovered quickly when combining with the Bi-doped ceria support. Then, O_2 reduction, thus regenerating hydroxide ions and closing the catalytic cycle, would be achieved by the Bi-doped ceria. There existed a large amount of oxygen vacancies in the Bi-doped ceria.[22, 29] O_2 tended to adsorb on these sites and became peroxide (OOH*) and hydrogen peroxide (HOOH*) intermediates through capturing hydrogen from H_2O.[33, 34] The decomposition of HOOH* to hydroxide could be catalyzed by the Pt NPs.[30] Moreover, some works indicated that bismuth was an active species towards the cleavage of the peroxide species.[35, 36] Despite the precise role of bismuth which was accompanied with the oxygen vacancy was not clear, it should be an important reason for the essential particularity of the Bi-doped ceria. Finally, electrons were captured by the hydroxide intermediates which were derived from the dissociation of the peroxide species and hydroxide ions were regenerated.[30, 32]

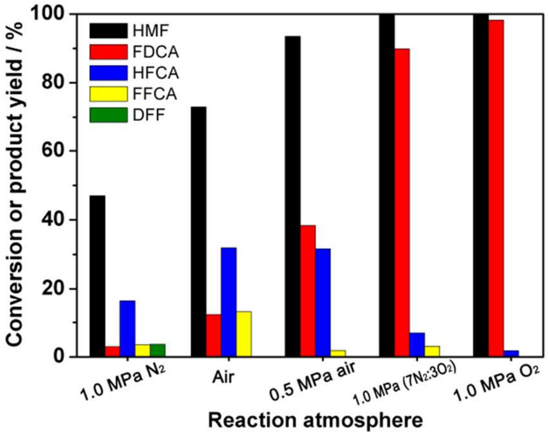
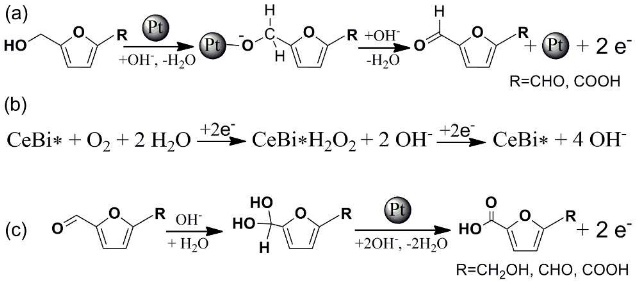


Fig. 5 HMF conversion and product yields at different reaction atmospheres over the Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst (Pt : HMF = 5×10^{-3} mol/mol, 4 equiv. NaOH, 23 °C, 30 min).

The effect of the O_2 concentration on the reaction over the Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst was examined and the results are shown in Fig. 5. Reaction under 1.0 MPa N_2 afforded a certain amount of products obtained from the oxidation of the alcohol group (FDCA, FFCA and DFF), which might ascribed to the presence of large amount of stoichiometric oxidant sites in the $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ support.[37] The yields of the oxidation products increased with the increasing concentration of O_2 and were limited with the low O_2 contents. It indicated that the O_2 reduction was a fast reaction process and the oxygen transfer limited this process when the O_2 concentration was low. For HMF oxidation catalyzed by the PVP stabilized Pt sol, O_2 concentration was identified not rate limiting, which matched the low reaction rate and catalytic activity.[27] In the presence of the Bi-doped ceria, the reaction rate increased greatly and high concentration O_2 was needed to capture the produced electrons and recover the catalyst timely.



Scheme 2 The proposed reaction mechanism for the oxidation of HMF in alkaline aqueous solution. CeBi* represented the oxygen vacancy accompanied with the bismuth.

The reaction mechanism was proposed in Scheme 2. With the Pt NPs and the Bi-doped ceria presented in the reaction system simultaneously, Pt-alkoxide intermediate was firstly formed with the help of the hydroxide ion in alkaline aqueous solution (Scheme 2a). Then, β-H elimination was achieved when the surface bound hydroxide intermediate captured the hydride which transferred from the C-H bond. These processes produced the aldehyde product and deposited two electrons on the Pt NPs. The electrons further transferred to molecular oxygen which adsorbed on the oxygen vacancy accompanied by bismuth. Finally, O_2 converted to hydroxide ions through the formation and dissociation of peroxide intermediate (Scheme 2b). The catalytic cycle completed and the catalyst recovered. This oxygen reduction process could not occur with the CeO_2 at the moderate reaction conditions. CeO_2 showed a lower redox activity at low temperature with a small amount of oxygen vacancies and the dissociation of the O-O bond of the formed peroxide intermediates might be inactive without bismuth. In addition, the aldehyde group of HMF, HFCA and FFCA underwent the similar oxidation processes after it hydrated to the geminal diol intermediate and FDCA was obtained finally. (Scheme 2c)

Thus, the Pt NPs provided the active sites for the generation of metal-alkoxide intermediate and then β-H elimination achieved. However, oxygen activation could not accomplish without an active support. The poor activity of the alcohol oxidation was resulted with Pt sol or Pt/CeO_2. The Bi-doped ceria has the capacity to transfer hydride and activate oxygen. But it could not activate the C-H bond in the alcohol group, which only resulted in the conversion of the aldehyde group and the production of HFCA and BHMF. When combining the Bi-doped ceria and Pt NPs, their functions were fitly combined and the efficient catalyst for HMF oxidation to FDCA was generated. Under the same conditions as Fig. 3, the same amounts of the Pt sol and $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ as that of the previous Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst were added into the reaction system separately, the reaction also resulted in a high 96% yield of FDCA after 30 min. It further identified that when catalyzing the oxidation of HMF to FDCA, the Pt sol and the $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ support played their own specific roles and their functions combined well.

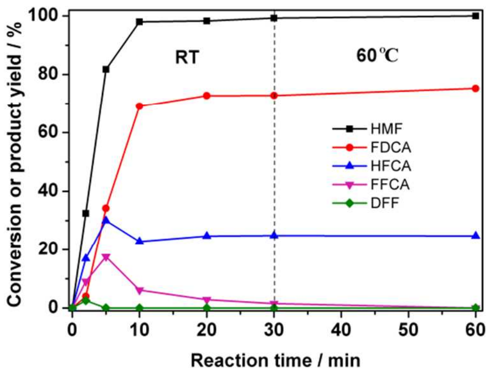


Fig. 6 HMF conversion and product yields as a function of reaction time at 23 °C for 30 min and 60 °C for another 30 min over 0.1 wt% Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst (Pt : HMF = 5×10^{-4} mol/mol, 4 equiv. NaOH, 1.0 MPa O_2).

The 98% high yield of FDCA was obtained only after 30 min over the most active Pt/$Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst at room temperature. Therefore, the loading amount of Pt was reduced to 0.1 wt% to further investigate the time course of the reaction. The result is shown in Fig. 6. Although the molar ratio of HMF to Pt was as high as 2000 in the reaction system, the catalyst showed excellent activity towards the oxidation of HMF. 98% conversion of HMF and 69% yield of FDCA were achieved only after 10 min. The TOF was calculated from the moles of HMF consumed in 5 min, normalized by the Pt atoms in the reactor. The value was 5.45 s^{-1}. It was much higher than the commercial Pt/C catalyst, which was examined in the oxidation of HMF in a previous work.[8] HMF was firstly oxidized to HFCA, DFF and FFCA which were further oxidized to FDCA (Fig. 6). There existed large amounts of HFCA and FFCA after 5 min, indicating that the oxidation of the alcohol group and the aldehyde group in HMF proceeded simultaneously and was both energetically favorable with the catalyst. In our previous work, however, a little FFCA and no DFF was detected in the reaction course over the $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$ catalyst.[22] It suggested that the oxidation of the alcohol group over the Pt catalyst was much easier than that over the Au catalyst.

Despite the conversions of HMF, HFCA and FFCA were very quick at the first 10 min, HFCA hardly transformed to FDCA after 20 min and a 73% yield of FDCA was finally obtained after 30 min. The reactor was then placed in an oil pot at 60 °C and reacted for another 30 min. The relative yields of HFCA and FDCA were nearly unchanged. It seemed that the catalyst became inactive after reaction. Then, the catalyst was recovered by centrifuging after reaction 30 min at room temperature and a new set of HMF oxidation experiment was carried out. HMF was also readily oxidized to the products within 30 min, suggesting that the catalyst was still active for the oxidation reaction after one catalytic cycle. The certain amount of HFCA which was inevitable in the final products might derive from some of the active sites in the catalyst being blocked by the products, which inhibited further oxidation of the alcohol group.

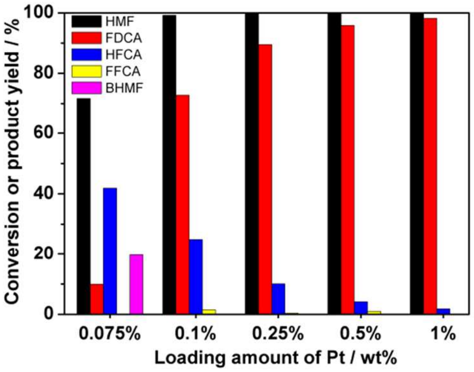


Fig. 7 HMF conversion and product yields over the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalysts with different loading amounts of Pt (0.0878 g catalyst, 4 equiv. NaOH, 1.0 MPa O_2, 23 °C, 30 min).

The influence of the loading amount of Pt (as well as the HMF/Pt molar ratio) on the product distribution was then investigated. The results shown in Fig. 7 illustrated that the selectivity to FDCA was improved by increasing the loading amount of Pt. It highlighted the viewpoint that Pt afforded the active sites for the generation of metal-alkoxide intermediate and then the oxidation of the alcohol group was achieved with the help of the hydroxide ions and the Bi-doped ceria. In addition, it was noteworthy that not only the conversion of HMF and the yield of FDCA decreased greatly when the loading amount of Pt reduced to 0.075%, but also the generation of nearly 20% yield of BHMF was occurred. BHMF was the product of the Cannizzaro reaction of HMF and $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ showed excellent catalytic activity towards this reaction.[22] It further implied that the natural properties of the $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ support were remained after depositing Pt NPs. The $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ support was capable for transferring hydride and activating oxygen and thus an active catalyst for converting HMF to HFCA and BHMF. However, when the loading amount of Pt was no less than 0.1 wt%, the oxidation reaction which also included the hydride transfer and oxygen activation procedures was the dominant reaction. The Cannizzaro reaction was inhibited and no BHMF was produced.

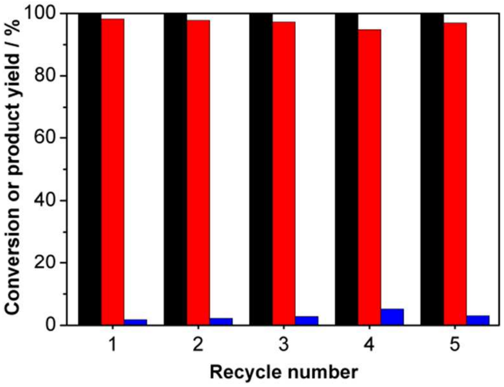


Fig. 8 Reusability study of 1 wt% $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst in the oxidation of HMF in aqueous solution (Pt : HMF = 5×10^{-3} mol/mol, 4 equiv. NaOH, 1.0 MPa O_2, 23 °C, 30 min; HMF: black, FDCA: red, HFCA: blue).

Finally, the catalyst recycling was studied for the 1 wt% $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst. After a reaction cycle, the catalyst was recovered by centrifuging and washing with water three times and used for another reaction cycle. The $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst could be reused for five times without significant loss of the activity under identical reaction conditions (Fig. 8). HMF was totally converted to oxidation products for all the reaction cycles and the FDCA yields were 98%, 98%, 97%, 95% and 97% in the 1st, 2nd, 3rd, 4th and 5th cycles, respectively. The filtrate after the first reaction cycle was analyzed by ICP analysis, the Pt content was 0.74 μg/ml, which corresponded nearly 0.5% Pt leaching. The amount was low and might be caused by the residual solid particles in the filtrate. After using five times, TEM analysis was conducted to examine the Pt morphology. No aggregation of Pt occurred and the size of Pt NPs was maintained well. All these results confirmed the superiority of the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst for the oxidation of HMF.

As the oxidation of HMF to FDCA contained an alcohol oxidation and an aldehyde oxidation, and the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst was efficient for the reaction at room temperature, we could imagine that the catalyst was also active for the oxidation of other alcohols or aldehydes.

Conclusions

In this work, Pt sol stabilized by PVP and the $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0, 0.1, 0.2, 0.5) supported Pt catalysts obtained by the sol-impregnation method were applied in the oxidation of HMF to FDCA at room temperature. The Pt/CeO_2 showed a poor catalytic performance towards the reaction, which was similar to the Pt sol. The $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst showed an excellent catalytic activity. 98% yield of FDCA was obtained over the $Pt/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ catalyst within 30 min and the catalyst was well reused for five times without much loss of the catalytic activity. An appropriate reaction mechanism was suggested. The natural properties of the Pt NPs and the ceria-based support were remained after their combination. The unique oxygen activation function of the Bi-doped ceria played an essential role during the catalytic oxidation process. It changed the performance of the ceria-based material supported Pt catalyst towards catalytic alcohol oxidation thoroughly. The catalyst should also be efficient for the oxidation of other alcohols or aldehydes at moderate reaction conditions. The catalytic activity could be further improved by modulating the Pt particle size.

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Notes and references

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