1. Introduction

Alcohol oxidation reaction is widely investigated in both laboratories and industrial applications due to the importance of its valuable products such as aldehydes and ketones, which are widely used in dyestuffs, polymer precursors, and pharmaceutical and agrochemical industries.\(^3\) Traditionally, stoichiometric oxidants such as dichromate or permanganate are used in the liquid phase oxidation but are toxic and expensive, which could not meet the development of green chemistry. Hence, there is a need of shifting from methods based on the toxic and inorganic oxidants to greener and more atom efficient methods which adopt molecular oxygen as oxidant.\(^4\)-\(^6\)

Considering that lots of noble metal catalysts have been used in the oxidation of alcohols using \(O_2\) as oxidant, Pd based catalysts have attracted much attention for its simple preparation method and excellent catalytic activity.\(^5\) However, some problems still impede its industrial applications. For example, the formation process of active phase is investigated elaborately for \(\text{Pd}/\text{SBA-15}\), but the agglomeration of the nanoparticles and low efficiency impede its applications.\(^6\)

To improve the catalytic activity of \(\text{Pd}\) catalyst, bimetal \(\text{Pd}\) based catalysts in alcohol oxidation reaction have attracted increasing interest in recent decades because they can finely tune the catalytic properties of metals. However, there are a lot of problems that still need to be solved. Reaction induced inactive \(\text{CuPd}\) alloy inhibits the reduction of highly active \(\text{Cu}_2\text{O}\) for \(\text{CuPd}–\text{Cu}_2\text{O}/\text{Ti}\) powder, but the conversion is lower than 90% at the temperature of 280 °C.\(^7\) The synergistic effect between \(\text{Au}\) and \(\text{Pd}\) species in \(\text{AuPd}/\text{TiO}_2\) is prominent in the oxidation of alcohols compared with \(\text{Au}/\text{TiO}_2\) or \(\text{Pd}/\text{TiO}_2\), but the tedious preparation process and the low efficiency impede its applications.\(^8\)-\(^11\)

Based on the problems mentioned above, the major challenge is to develop an effective catalyst endowed with high activity at low temperature coupled with high thermal conductivity to enhance the catalyst stability.\(^6\) \(\text{SiC}\) powder is chosen as support because of its excellent heat conductivity, low price and high oxidation/corrosion resistance behavior.\(^3\) The synergistic effect between \(\text{Pd}\) and oxides such as \(\text{Cu}_2\text{O}\) has been reported,\(^4\) but the reaction temperature is still high and the reaction induced process (the alcohol could convert inactive fresh catalyst into active catalyst) has not been discussed. As a continuation of our previous research, \(\text{in situ}\) reaction induced \(\text{PdBi}/\text{SiC}\) catalyst is prepared by a simple impregnation and calcination method. The transformation from \(\text{PdO}–\text{Bi}_2\text{O}_3\) to \(\text{Pd}^0–\text{Bi}_2\text{O}_3\) is confirmed, which is testified by XRD and XPS. The synergism between \(\text{Pd}\) and \(\text{Bi}_2\text{O}_3\) is prominent due to excellent catalytic activity of \(\text{PdBi}/\text{SiC}\) and the inferior catalytic activities of \(\text{PdSiC}\) or \(\text{BiSiC}\).

2. Experimental section

2.1 Materials and methods

\(\text{SiC}\) powder (200–300 mesh with surface area of 0.15 m\(^2\) g\(^{-1}\)), \(\text{Pd(NO}_3\text{)}_2\cdot2\text{H}_2\text{O}\) and \(\text{Bi(NO}_3\text{)}_3\cdot5\text{H}_2\text{O}\) were purchased from Sinopharm Chemical Reagent Co Ltd. SBA-15 and MCM-41 were supplied by Nankai University Catalyst Co Ltd. Other substrates were supplied by Aladdin Reagent Co. Ltd. All catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP Thermo
2.2 Preparation of the catalysts

Pd$_3$Bi$_5$/SiC fresh (weight loading of Pd and Bi was 3 wt% and 5 wt% respectively) was prepared by impregnation of 1 g SiC powder, 65 mg Pd(NO$_3$)$_2$$\cdot$2H$_2$O, 116 mg Bi(NO$_3$)$_3$$\cdot$5H$_2$O and 2 mL H$_2$O followed by being dried at 100 °C overnight and calcinated at 300 °C in air for 2 h, which was denoted as Pd$_3$Bi$_5$/SiC fresh. Additionally, other catalysts such as Pd$_3$Bi$_5$/SiC fresh, Pd$_y$/SiC fresh and Bi$_y$/SiC fresh (x and y indicate the weight content of Pd and Bi respectively) were prepared following the same procedure by simply tuning the weight of Pd(NO$_3$)$_2$$\cdot$2H$_2$O or Bi(NO$_3$)$_3$$\cdot$5H$_2$O. The fresh catalysts (Pd$_x$/Bi$_y$/SiC fresh, Pd$_y$/SiC fresh and Bi$_y$/SiC fresh) after 1 h running (Time on steam (TOS) of 1 h) in the reaction conditions (see Section 2.3, catalytic tests) were denoted as Pd$_x$/Bi$_y$/SiC, Pd$_y$/SiC and Bi$_y$/SiC for short.

2.3 Catalytic tests

The gas phase selective oxidation process was carried out on a fixed-bed reactor (inner diameter of 10 mm) under atmospheric pressure made up by ourselves (Scheme S1†). Catalyst used in each experiment was 0.3 g (200–300 mesh) and alcohols are fed continuously by a peristaltic pump, in parallel with O$_2$ (oxidant) and N$_2$ (dilute gas) feeding using the calibrated mass flow controllers, into the reactor heated to 240 °C. WHSV (weight hourly space velocity) of alcohol was 20 h$^{-1}$ and the molecular ratio of alcohol/O$_2$/N$_2$ is 1/0.6/2.4. The products were analysed by Gas Chromatography (SP-7820 with TCD detector). The calculation method of benzyl alcohol conversion and benzaldehyde selectivity were listed in the ESI.† All the catalytic tests were repeated for 3 times to improve accuracy.

In order to prevent the oxidation of our catalysts after reaction, the spent catalysts are collected until cooling down to room temperature under the protection of N$_2$.

### 3. Results and discussion

#### 3.1 Catalytic activity

The catalytic activities of the catalysts are shown in Table 1. Given the strong exothermic effect in the gas phase oxidation of alcohol, the chemically inert SiC powder with excellent thermal conductivity and high oxidation resistance behaviour other than oxides (such as Al$_2$O$_3$ and TiO$_2$) or zeolites (such as SBA-15) is selected as supports (Table 1, entry 1). The catalytic behaviour of pure Pd$_x$/SiC catalysts is very low (Table 1, entries 2 and 3), which is in accordance with previously reported Pd/Ti powder catalyst.† It is noted that Bi$_y$/SiC catalyst is nearly inactive in alcohol oxidation even with Bi content increasing to 5% (Table 1, entries 4 and 5). At 280 °C, the conversion of benzyl alcohol increases from 90% to 95% with Pd loading increasing from 1% to 2% (Table 1, entries 6 and 8) for Pd$_x$/Bi$_y$/SiC catalyst, which is nearly unchanged with Pd loading further increasing to 3% (Table 1, entry 10). As for Pd$_x$/Bi$_y$/SiC catalysts, further increasing the Pd content to 4% or 5% does not yield better performance (Table 1, entries 16 and 17), indicating that there may be

| Entry | Catalyst | Content of Pd$^d$ (wt%) | Content of Bi$^d$ (wt%) | Conversion$^e$ (%) | Selectivity$^f$ (%) |
|-------|----------|--------------------------|--------------------------|-------------------|-------------------|
| 1     | SiC      | 0                        | 0                        | 3                 | 97                |
| 2     | Pd$_x$/SiC | 0.96                     | 0                        | 11                | 98                |
| 3     | Pd$_y$/SiC | 4.68                     | 0                        | 31                | 99                |
| 4     | Bi$_x$/SiC | 0                       | 0.88                     | 2                 | 98                |
| 5     | Bi$_y$/SiC | 0                       | 4.70                     | 6                 | 97                |
| 6     | Pd$_x$/Bi$_y$/SiC | 0.90 | 4.68 | 90 | 97 | 97 |
| 7$^a$ | Pd$_y$/Bi$_x$/SiC | 0.90 | 4.68 | 78 | 98 | 98 |
| 8     | Pd$_x$/Bi$_y$/SiC | 1.82 | 4.81 | 95 | 98 | 98 |
| 9$^a$ | Pd$_y$/Bi$_y$/SiC | 1.82 | 4.81 | 88 | 98 | 98 |
| 10    | Pd$_x$/Bi$_x$/SiC | 2.90 | 4.52 | 98 | 97 | 98 |
| 11$^a$ | Pd$_y$/Bi$_y$/SiC | 2.90 | 4.52 | 93 | 98 | 98 |
| 12$^a$ | Pd$_x$/SiC&Bi$_y$/SiC | 2.71 | 4.83 | 25 | 97 | 97 |
| 13$^b$ | CuPd–Cu$_3$O/Ti | 3.10 | 0 | 65 | 99 |
| 14    | Pd/TiO$_2$ | 0.7 | 0 | 50 | 98 | 98 |
| 15    | Pd/SBA-15 | 1.0 | 0 | 99 | 99 |
| 16    | Pd$_x$/Bi$_x$/SiC | 3.8 | 4.89 | 97 | 95 |
| 17    | Pd$_x$/Bi$_y$/SiC | 4.9 | 4.92 | 97 | 96 |

$^a$ Reaction conditions: catalyst 300 mg, temperature 280 °C, O$_2$/alcohol/N$_2$ = 0.6/1/2.4 and WHSV 20 h$^{-1}$. $^b$ Temperature 240 °C. $^c$ Pd$_x$/SiC and Bi$_y$/SiC are physically mixed. $^d$ The content is confirmed by ICP. $^e$ Conversion of benzyl alcohol. $^f$ Selectivity of benzaldehyde.
sufticient Pd0–Bi2O3 interface in the reaction. So Pd3Bi5/SiC is selected as the optimal catalyst given to its excellent catalytic activity and thermal conductivity, which exhibits remarkable performance compared with previously reported Pd based catalysts. Anti-sintered large size Pd particles show inferior catalytic activity compared with aforementioned catalysts (Table 1, entry 14). For benzyl alcohol oxidation at 240 °C, Pd3Bi5/SiC delivers a single run life time of 200 hours with excellent activity and selectivity (Fig. 1). For aromatic alcohols, such as 1-phenylethanol and 2-phenylethanol, the conversion is 75% and 55% respectively and the selectivity of phenylacetaldehyde and acetophenone is 98% and 97% respectively. For methanol and ethanol, the conversion is 91% and 88% respectively (Table S1†).

3.2 Physicochemical characterization of fresh Pd3Bi5/SiC catalyst

In order to further identify the active site in the reaction, Pd3Bi5/SiC fresh is characterized elaborately by XRD and XPS because valance effect other than particle size or surface area plays an important role in the gas phase oxidation of alcohols.12,13 XRD and XPS indicate that PdO and Bi2O3 are formed after calcination of nitrate salts with SiC powder. Given the weak characteristic diffraction peaks of PdO centered at 2θ = 31.5° (Fig. 2A), we conclude that the particle size is very small, which is in accordance with the previous report.7 Just like PdO nanoparticles, the small size Bi2O3 nanoparticles are formed given the weak characteristic diffraction peak centered at 2θ = 27.4° (Fig. 2B). The binding energy of Bi is centered at 160.0 eV, which is much higher than that of metallic Bi (Fig. 2C).14,15 Hence, the electron transfer from Bi to O is prominent and Bi2O3 is formed in the pre-treatment conditions. Just like Pd3Bi5/SiC fresh, PdO and Bi2O3 are formed for Pd3/SiC fresh and Bi5/SiC fresh respectively (Fig. 2A).

3.3 Formation of active site and the influence of supports

Compared with Pd3/SiC and Bi5/SiC, reaction induced Pd0–Bi2O3 species from PdO–Bi2O3 in the reaction conditions plays an important role in the catalytic activity (Table 1, entries 3, 5 and 11), which is verified by XRD, TEM and XPS. XRD pattern indicates that the diffraction peak of Bi2O3 remains unchanged while the diffraction peak of PdO disappears and the new diffraction peaks of Pd form compared with Pd3Bi5/SiC fresh.

**Table 2** Influence of supports

| Catalyst           | ΔT° (°C) | Conversion* (%) | Conversion† (%) |
|--------------------|---------|----------------|-----------------|
| Pd3Bi5/SiC         | 6       | 98             | 90              |
| Pd3Bi5/Al2O3       | 32      | 93             | 68              |
| Pd3Bi5/TiO2        | 25      | 96             | 75              |
| Pd3Bi5/SiO2        | 36      | 93             | 65              |
| Pd3Bi5/SBA-15      | 30      | 95             | 72              |

* Reaction conditions: catalyst 300 mg, temperature 240 °C, O2/alcohol/N2 = 0.6/1/2.4 and WHSV 20 h⁻¹. ΔT is the temperature difference between catalyst bed and reactor external wall. * Conversion of benzyl alcohol after 2 h running. † Conversion of benzyl alcohol after 20 h running.
Pd 2p spectrum indicates that the strong binding energy peak at 335.3 eV is prominent, so Pd\(^0\) is formed in the reaction conditions (Fig. 3B).\(^4,4\) The binding energy of Bi 2p is close to that of the fresh catalyst, so XRD and XPS indicate that Bi\(_2\)O\(_3\) remains unchanged in the reaction conditions (Fig. 3C). TEM indicates that the ensembles consist of the small size 5.8 nm Pd\(^0\) or Bi\(_2\)O\(_3\) nanoparticles (Fig. 3D). The lattice fringes of Pd nanoparticle and Bi\(_2\)O\(_3\) nanoparticle are 0.225 nm and 0.326 nm respectively, which is in accordance with XRD results and the previous reports (Fig. 3E and F).\(^6,14,15\) The mapping images indicate that Pd, Bi and O distribute on the support randomly and the agglomeration of the nanoparticles is inhibited after the reaction conditions (Fig. 3G–I). Furthermore, TEM images show that the particle sizes of used Pd\(_3\)/SiC and Bi\(_5\)/SiC catalysts are 5.5 and 6.5 nm respectively, so the influence of particle size effect on the catalytic activity could be excluded (Fig. S1†). Moreover, TG curve shows that the carbon content is lower than 2 wt%, showing the excellent thermal conductivity of SiC powder (Fig. S1†). In order to further testify the active phase in the oxidation of benzyl alcohol, other supports such as Al\(_2\)O\(_3\), TiO\(_2\), SBA-15, SiO\(_2\) and MCM-41 are used to prepare the catalysts. Interestingly, Pd\(_3\)Bi\(_5\)/Al\(_2\)O\(_3\), Pd\(_3\)Bi\(_5\)/TiO\(_2\), Pd\(_3\)Bi\(_5\)/SiO\(_2\), Pd\(_3\)Bi\(_5\)/SBA-15 and Pd\(_3\)Bi\(_5\)/MCM-41 all exhibit excellent catalytic activities in the first 2 h running (Table 2). However, the conversion of benzyl alcohol decreases rapidly after 20 h running in the reaction conditions. The catalyst bed packed with Pd\(_3\)Bi\(_5\)/SiC delivers a low \(\Delta T\) (the temperature difference between catalyst bed and reactor external wall) of 6 °C at 240 °C, which is much lower than that of other catalysts (Table 2). So Pd\(_3\)Bi\(_5\)/SiC exhibits excellent heat conductivity in the low temperature gas phase oxidation of alcohols, which helps in rapidly dissipating the great quantity of reaction heat liberated from such strongly exothermic process and the influence of supports is ruled out for the oxidation of alcohols.\(^13\)

### 3.4 Further discussions of active Pd\(^0\)-Bi\(_2\)O\(_3\) and inactive PdO-Bi\(_2\)O\(_3\) phase

For the fresh and used Pd\(_3\)Bi\(_5\)/SiC catalyst, XRD and XPS results indicate that PdO–Bi\(_2\)O\(_3\) and Pd\(^0\)-Bi\(_2\)O\(_3\) ensembles are the main

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**Fig. 3** (A) XRD patterns of the Pd\(_3\)/SiC, Bi\(_5\)/SiC and Pd\(_3\)Bi\(_5\)/SiC; (B) Pd 2p spectrums of Pd\(_3\)/SiC and Pd\(_3\)Bi\(_5\)/SiC; (C) Bi 2p spectrums of Bi\(_5\)/SiC and Pd\(_3\)Bi\(_5\)/SiC; (D) TEM image of Pd\(_3\)Bi\(_5\)/SiC; (E) lattice fringe of Pd in Pd\(_3\)Bi\(_5\)/SiC; (F) lattice fringe of Bi\(_2\)O\(_3\) in Pd\(_3\)Bi\(_5\)/SiC; (E–G) distributions of Pd, Bi and O in Pd\(_3\)Bi\(_5\)/SiC.
phase in the catalyst (Section 3.2 and 3.3). Hence, reductive alcohol reduces inactive PdO–Bi2O3 to active Pd0–Bi2O3. To further compare between the catalytic efficiency of PdO–Bi2O3 and Pd0–Bi2O3, we compare the catalytic activities of the catalysts in the reaction conditions after different time on steam (TOS).16 XPS results show that the binding energy peaks at 335.0 and 336.4 eV are attributed to Pd0 and PdO respectively (Fig. 4A). After calcinations at 300 °C, Pd species for Pd3Bi5/SiC exist in the form of PdO phase (Fig. 2A). The conversion of alcohol increases and the ratio of Pd0/PdO increases with the prolongation of TOS. For example, after 10 minutes running in the reaction conditions, Pd0/PdO ratio is 52% and the conversion of alcohol is 63% (Fig. 4A).4 Similarly, Pd0/PdO ratio is 73% and the conversion of alcohol is 78% after 20 minutes running in the reaction conditions (Fig. 4A).

Interestingly, PdO disappears and Pd is dominant for Pd3Bi5/SiC (TOS of 1 h) (Fig. 3A). XRD results show that the diﬀraction peaks of PdO decreases and the ratio of Pd0/PdO ratio is 52% and the conversion of alcohol is 63% (Fig. 4A).4 Similarly, Pd0/PdO ratio is 73% and the conversion of alcohol is 78% after 20 minutes running in the reaction conditions (Fig. 4A).

Lots of techniques should be adopted to investigate the synergistic effect between Pd and Bi2O3. For the gas phase alcohol oxidation reaction, catalytic and oxidative dehydrogenation are the main routes. For the catalytic dehydrogenation mechanism, the H atom in the alcohol will be captured by the oxides, which will be moved by oxygen with the aid of metals. However, for the oxidative dehydrogenation mechanism, active oxygen species will be participated into the Mars Krevelen mechanism.17,18

Just like Cu-based catalysts, to further confirm the catalytic oxidation cycle, solid state 1H NMR is used to characterize the Bi2O3–H species. Four catalysts, Pd3Bi5/SiC (a), Pd3Bi5/SiC reacted with benzyl alcohol in the absence of O2 at 240 °C for 2 h (b), Bi5/SiC (c), Bi5/SiC reacted with benzyl alcohol in the absence of O2 at 240 °C for 2 h (d) are used to probe the Bi2O3–H species. The 1H NMR signal at 1.3 and 4.9 pm are corresponding with Bi2O3–H and H2O (Fig. 5). For the catalysts (b) and (d), the similar strong hydride NMR peaks are obtained, showing their similar catalytic dehydrogenation activity. However, the Bi2O3–H signal decreases obviously on Pd3Bi5/SiC (Aa/Ab = 0.30), while decreases slightly over Bi5/SiC (Aa/Ab = 0.82).

In the end, the TOF values of Pd3Bi5/SiC and Pd3/SiC are calculated (Table S2†). In the experiments, the WHSVs are optimized to obtain the low benzyl alcohol conversion. The TOF values of Pd3Bi5/SiC is 8842 and 2210 h−1 at 260 and 240 °C respectively, which are about 43 and 34 times of that of Pd3/SiC.

However, the chemical absorbed oxygen could be detected by O2-TPD and the conversion of alcohol will be about 1–2% in the absence of O2 for the oxidative dehydrogenation system. Hence, absorbed oxygen species plays an important role in the oxidative dehydrogenation other than catalytic dehydrogenation.17,18

To differentiate the two mechanisms over Pd3Bi5/SiC catalyst, the control experiments in the absence of O2 are conducted firstly. The conversions of benzyl alcohol are about 7–9% at 240 °C for Bi5/SiC and Pd3Bi5/SiC. Secondly, O2-TPD shows there are no O2 desorption peaks on the two catalysts (Fig. S2†). So the catalytic oxidation cycle is tentatively proposed.
4. Conclusions

Pd₃Bi₅/SiC was successfully prepared in a simple impregnation method, which shows excellent activity and stability in alcohol oxidation reaction. In the reaction conditions, benzyl alcohol reduces the inactive PdO–Bi₂O₃ to active Pd⁰–Bi₂O₃, which plays an important role in the low temperature gas phase oxidation of alcohols. XRD, XPS and control experiments indicate that Pd⁰/PdO ratio was vital for this reaction. Control experiments, O₂-TPD and ¹H NMR testify that Pd⁰–Bi₂O₃ is beneficial to eliminating the Bi₂O₃–H intermediates.

Conflicts of interest

There are no conflicts to declare.

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