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Reaction induced robust Pd_xBi_y/SiC catalyst for the gas phase oxidation of monopolistic alcohols†

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Reaction induced Pd_xBi_y/SiC catalysts exhibit excellent catalytic activity (92% conversion of benzyl alcohol and 98% selectivity of benzyl aldehyde) and stability (time on stream of 200 h) in the gas phase oxidation of alcohols at a low temperature of 240 °C due to the formation of Pd⁰-Bi₂O₃ species. TEM indicates that the agglomeration of the 5.8 nm nanoparticles is inhibited under the reaction conditions. The transformation from inactive PdO-Bi₂O₃ to active Pd⁰-Bi₂O₃ under the reaction conditions is confirmed elaborately by XRD and XPS.

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.^{1–3} 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 O₂ as oxidant, Pd based catalysts have attracted much attention for its simple preparation method and excellent catalytic activity.⁴ However, some problems still impede its industrial applications. For example, the formation process of active phase is investigated elaborately for Pd/SBA-15, but the agglomeration of the nanoparticles and low efficiency are inevitable.⁷ Pd/Al₂O₃ is reported by Li *et al.*, however, the reduction of active PdO to inactive Pd⁰ in the reaction conditions contributes to the deactivation of the catalyst.^{8,9} Sulfur doped SBA-15 supported Pd exhibits excellent catalytic activity, however, the instability of the amorphous Pd is adverse in industrial applications.² Novel highly stable and anti-sintered large size Pd/TiO₂ for the oxidation of benzyl alcohol has been reported, but the conversion of benzyl alcohol is lower than 50%.³

To improve the catalytic activity of Pd catalyst, bimetal 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 CuPd alloy inhibits the reduction of highly active Cu₂O for CuPd-Cu₂O/Ti powder, but the conversion is lower than 90% at the temperature of 280 °C.⁴ The synergistic effect between Au and Pd species in AuPd/TiO₂ is prominent in the oxidation of alcohols compared with Au/TiO₂ or Pd/TiO₂, but the tedious preparation process and the low efficiency impede its applications.^{10,11}

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 SiC powder is chosen as support because of its excellent heat conductivity, low price and high oxidation/corrosion resistance behavior.⁵ The synergistic effect between Pd and oxides such as Cu₂O 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, *in situ* reaction-induced Pd₃Bi₅/SiC catalyst is prepared by a simple impregnation and calcination method. The transformation from PdO-Bi₂O₃ to Pd⁰-Bi₂O₃ is confirmed, which is testified by XRD and XPS. The synergism between Pd and Bi₂O₃ is prominent due to excellent catalytic activity of PdBi/SiC and the inferior catalytic activities of Pd/SiC or Bi/SiC.

2. Experimental section

2.1 Materials and methods

SiC powder (200–300 mesh with surface area of 0.15 m² g⁻¹), Pd(NO₃)₂·2H₂O and Bi(NO₃)₃·5H₂O 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 spectrometry (ICP-AES, ICP Thermo

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IRIS Intrepid II XSP; USA), X-ray photoelectron spectroscopy (XPS, Escalab 250xi spectrometer, Al K α , adventitious C 1s line (284.8 eV) as the reference), X-ray diffraction (XRD, Rigaku Ultima IV diffractometer with Cu K α radiation (35 kV and 25 mA); Japan), scanning electron microscopy (SEM, Hitachi S-4800; Japan) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK), O₂-temperature programmed desorption (O₂-TPD) measurements were performed on a Quanta chrome ChemBET 3000 (USA) chemisorption apparatus with a thermal conductivity detector (TCD), and transmission electron microscopy (TEM, FEI-Tecnaï G2 F30; USA). ¹H NMR spectra were recorded on a Bruker 400 or a Agilent 400 (100 MHz).

2.2 Preparation of the catalysts

Pd₃Bi₅/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(NO₃)₂·2H₂O, 116 mg Bi(NO₃)₃·5H₂O and 2 mL H₂O followed by being dried at 100 °C overnight and calcinated at 300 °C in air for 2 h, which was denoted as Pd₃Bi₅/SiC fresh. Additionally, other catalysts such as Pd_xBi_y/SiC fresh, Pd_x/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(NO₃)₂·2H₂O or Bi(NO₃)₃·5H₂O. The fresh catalysts (Pd_xBi_y/SiC fresh, Pd_x/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_xBi_y/SiC, Pd_x/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 O₂ (oxidant) and N₂ (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/O₂/N₂ 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 N₂.

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 Al₂O₃ and TiO₂) 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.⁴ 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_xBi₅/SiC catalyst, which is nearly unchanged with Pd loading further increasing to 3% (Table 1, entry 10). As for Pd_xBi₅/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

Table 1 Catalytic activity of the catalysts^a

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

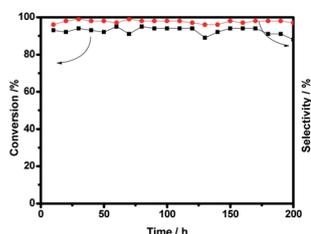
^a Reaction conditions: catalyst 300 mg, temperature 280 °C, O₂/alcohol/N₂ = 0.6/1/2.4 and WHSV 20 h⁻¹. ^b Temperature 240 °C. ^c Pd₃/SiC and Bi₅/SiC are physically mixed. ^d The content is confirmed by ICP. ^e Conversion of benzyl alcohol. ^f Selectivity of benzaldehyde.



Table 2 Influence of supports^a

Catalyst	ΔT^b (°C)	Conversion ^c (%)	Conversion ^d (%)
Pd ₃ Bi ₅ /SiC	6	98	90
Pd ₃ Bi ₅ /Al ₂ O ₃	32	93	68
Pd ₃ Bi ₅ /TiO ₂	25	96	75
Pd ₃ Bi ₅ /SiO ₂	36	93	65
Pd ₃ Bi ₅ /SBA-15	30	95	72

^a Reaction conditions: catalyst 300 mg, temperature 240 °C, O₂/alcohol/N₂ = 0.6/1/2.4 and WHSV 20 h⁻¹. ^b ΔT is the temperature difference between catalyst bed and reactor external wall. ^c Conversion of benzyl alcohol after 2 h running. ^d Conversion of benzyl alcohol after 20 h running.

Fig. 1 Long-term test for the Pd₃Bi₅/SiC catalyst.

sufficient 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. However, the catalytic activity of Pd₃Bi₅/SiC is much higher than that of Pd₁Bi₅/SiC and Pd₂Bi₅/SiC at the lower temperature of 240 °C (Table 1, entries 7, 9 and 11).

Interestingly, the conversion of benzyl alcohol is just 25% when Pd₃/SiC and Bi₅/SiC are physically mixed (Table 1, entry 12), which is similar to the previously reported Ag_{2.5}Cu₅/SiC catalyst.⁶ So Pd₃Bi₅/SiC exhibits excellent heat conductivity in the low temperature gas phase oxidation of alcohols. Furthermore, the influence of support in this reaction could be neglected (Table 2). Thus Pd₃Bi₅/SiC is selected as the optimal catalyst given 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).³ 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 $2\theta = 31.5^\circ$ (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 $2\theta = 27.4^\circ$ (Fig. 2A). Pd 2p spectrum indicates that the binding energy peak at 336.6 eV is assigned to PdO^{2,3,8} (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

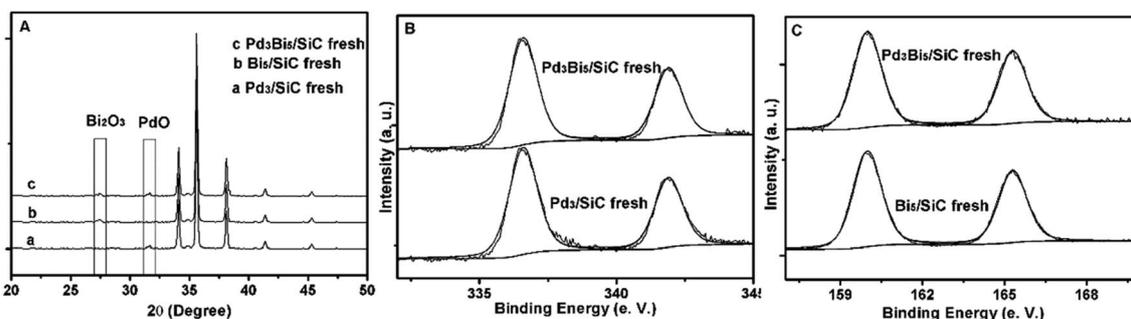


Fig. 2 (A) XRD patterns of the Pd₃/SiC fresh, Bi₅/SiC fresh and Pd₃Bi₅/SiC fresh; (B) Pd 2p spectrums of Pd₃/SiC fresh and Pd₃Bi₅/SiC fresh; (C) Bi 2p spectrums of Bi₅/SiC fresh and Pd₃Bi₅/SiC fresh.



(Fig. 3A). Pd 2p spectrum indicates that the strong binding energy peak at 335.3 eV is prominent, so Pd⁰ is formed in the reaction conditions (Fig. 3B).^{3,4} The binding energy of Bi 2p is close to that of the fresh catalyst, so XRD and XPS indicate that Bi₂O₃ remains unchanged in the reaction conditions (Fig. 3C). TEM indicates that the ensembles consist of the small size 5.8 nm Pd⁰ or Bi₂O₃ nanoparticles (Fig. 3D). The lattice fringes of Pd nanoparticle and Bi₂O₃ 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).^{4,14,15} 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 Pd₃/SiC and Bi₅/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 Al₂O₃, TiO₂, SBA-15, SiO₂ and MCM-41 are used to prepare the catalysts. Interestingly, Pd₃Bi₅/Al₂O₃, Pd₃Bi₅/TiO₂, Pd₃Bi₅/SiO₂, Pd₃Bi₅/SBA-15 and Pd₃Bi₅/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 Pd₃Bi₅/SiC delivers a low Δ*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 Pd₃Bi₅/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 Pd⁰-Bi₂O₃ and inactive PdO-Bi₂O₃ phase

For the fresh and used Pd₃Bi₅/SiC catalyst, XRD and XPS results indicate that Pd⁰-Bi₂O₃ and Pd⁰-Bi₂O₃ ensembles are the main

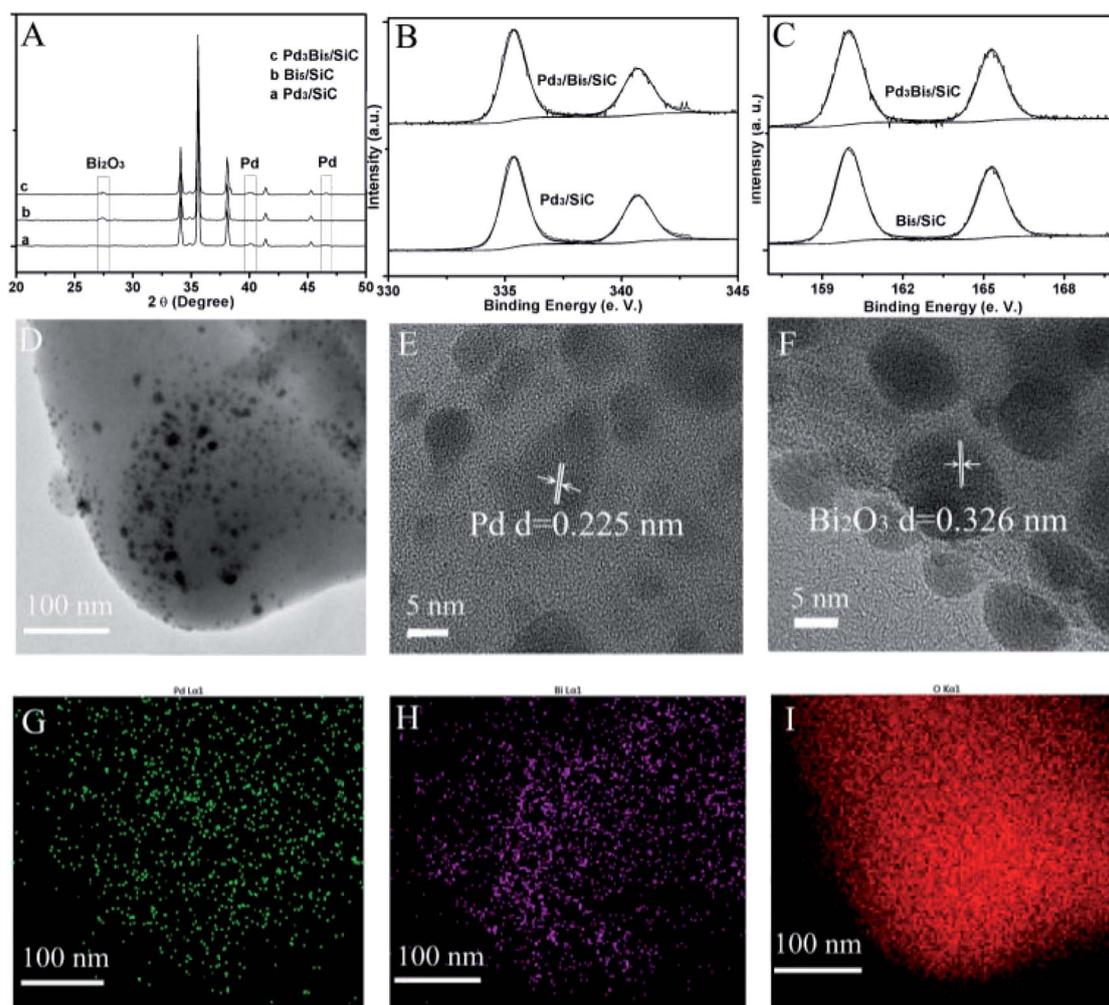


Fig. 3 (A) XRD patterns of the Pd₃/SiC, Bi₅/SiC and Pd₃Bi₅/SiC; (B) Pd 2p spectrums of Pd₃/SiC and Pd₃Bi₅/SiC; (C) Bi 2p spectrums of Bi₅/SiC and Pd₃Bi₅/SiC; (D) TEM image of Pd₃Bi₅/SiC; (E) lattice fringe of Pd in Pd₃Bi₅/SiC; (F) lattice fringe of Bi₂O₃ in Pd₃Bi₅/SiC; (E–G) distributions of Pd, Bi and O in Pd₃Bi₅/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 shows 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 exists 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 peak of PdO decreases and the diffraction peaks of Pd⁰ increase with the prolongation of reaction time, which is corresponding with XPS results (Fig. 4B). Interestingly, it can be seen that the conversion of benzyl alcohol increases linearly with the Pd⁰/PdO ratio (Fig. 4C). The diffraction peaks of support and Bi₂O₃ remain unchanged (Fig. 4B). However, given the low catalytic activity of Pd₃/SiC and Bi₅/SiC, Pd⁰ or Bi₂O₃ is inactive in alcohol oxidation (Table 1, entries 3 and 5, Fig. 3A). Hence, XRD and XPS indicate that 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.

3.5 Synergistic effect between Pd and Bi₂O₃

Lots of techniques should be adopted to investigate the synergistic effect between Pd and Bi₂O₃. Reportedly, for the gas phase alcohol oxidation reaction, catalytic and oxidative dehydration 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}

The chemical absorbed oxygen couldn't be detected by O₂-TPD and the conversion of alcohol will be about 5–10% in the absence of O₂ for the catalytic dehydrogenation system.

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.

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 ppm are corresponding with Bi₂O₃–H and H₂O (Fig. 5). For the catalysts (b) and (d), the similar strong hydride HNMR peaks are obtained, showing their similar catalytic dehydrogenation activity. However, the Bi₂O₃–H signal decreases obviously on Pd₃Bi₅/SiC (A_a/A_b = 0.30), while decreases slightly over Bi₅/SiC (A_a/A_b = 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. So the results mentioned above testify that Pd⁰–Bi₂O₃ is beneficial to eliminating the Bi₂O₃–H intermediates.

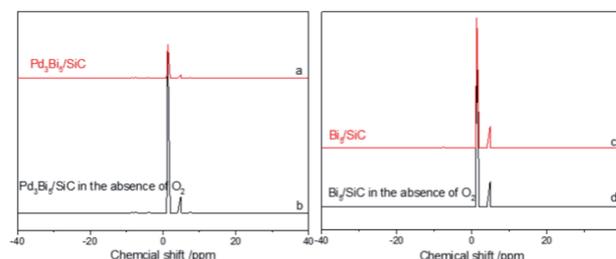


Fig. 5 ¹H NMR spectra of the catalysts.

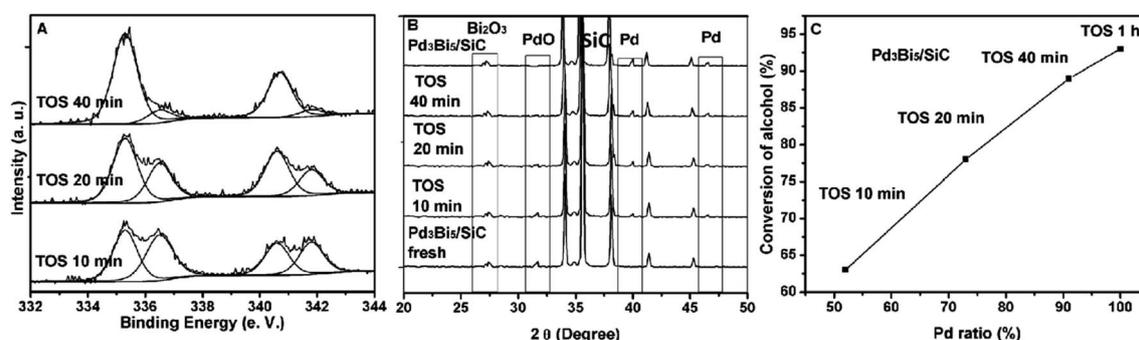


Fig. 4 (A) Pd 2p spectra of Pd₃Bi₅/SiC (TOS of 10, 20 and 40 minutes); (B) XRD patterns of Pd₃Bi₅/SiC (TOS of 10, 20 and 40 minutes); (C) catalytic activity of Pd₃Bi₅/SiC (TOS of 10, 20 and 40 minutes).



4. Conclusions

$\text{Pd}_3\text{Bi}_5/\text{SiC}$ 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 $\text{PdO}-\text{Bi}_2\text{O}_3$ to active $\text{Pd}^0-\text{Bi}_2\text{O}_3$, which plays an important role in the low temperature gas phase oxidation of alcohols. XRD, XPS and control experiments indicate that Pd^0/PdO ratio was vital for this reaction. Control experiments, O_2 -TPD and ^1H NMR testify that $\text{Pd}^0-\text{Bi}_2\text{O}_3$ is beneficial to eliminating the $\text{Bi}_2\text{O}_3-\text{H}$ intermediates.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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