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Enhanced activity and stability of Zr-promoted Pd/HZSM-5 catalyst for low-temperature methane combustion†

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A Zr-promoted Pd/HZSM-5 catalyst, prepared by an impregnation method, was found to possess high catalytic activity as well as thermal and hydrothermal stability for low-temperature methane combustion.

In recent years, there has been increasing interest in the low-temperature methane (CH_4) combustion technology, which is extensively used in the catalytic oxidation of diluted CH_4 for energy generation and exhaust gas treatment.[1–3] In spite of the efforts to search for non-noble metal catalysts as less costly alternatives, Pd-related catalysts are still considered as the most active for CH_4 combustion.[4–6] However, in practical exhaust streams, the catalyst must ignite reaction below 300 °C, oxidise nearly 100% of CH_4 below 400 °C, and show a good catalytic lifetime.[7–8] Conventional Pd-supported catalysts, *e.g.*, Pd/Al_2O_3,[9] were found to be not efficient enough for this catalytic process. Pd-supported zeolite catalysts, such as Pd/HZSM-5[10,11] and Pd/SAPO-5,[12] show excellent low-temperature activity and conversion efficiency for CH_4 combustion. However, these catalysts, which are typically prepared by the ion-exchange method, show poor thermal and hydrothermal stabilities. There is a general agreement that the activity of Pd catalysts is affected by the types of supports and additives. The promotion effects of Zr, Y, La and Al on Pd-supported catalysts have been reported for catalytic oxidation of hydrocarbons.[13–16] In this work, we report on the preparation of a series of pure and modified Pd/HZSM-5 catalysts using the impregnation method, and the promoting effects of additives on the CH_4 oxidation activity of Pd/HZSM-5.

First, M/HZSM-5 (Si/Al_2 = 165, M = Zr, Y, La and Al) supports were prepared by impregnating the parent HZSM-5 powders for 12 h with aqueous solutions of the corresponding nitrate salts, respectively, followed by drying at 120 °C for 12 h and calcining at 500 °C for 3 h. Then, the powders obtained were impregnated with $Pd(NO_3)_2$ aqueous solution. Pure and modified Pd/HZSM-5 catalysts were obtained after repeating the above drying and calcining procedures. For comparison, Pd/γ-Al_2O_3 and Pd/SiO_2 samples were also similarly prepared. The desired loading of all the metals in their metallic states were 1 wt% of the catalysts.

The catalytic activity and lifetime tests of the catalysts were carried out using a tubular quartz microreactor of the down-flow fixed-bed type at atmospheric pressure. A powder sample of 100 mg (45–60 mesh) was placed on the reaction bed, and the reaction mixture of CH_4, O_2 and N_2 (2 : 8 : 90 vol%) was fed into the reactor at a space velocity of 48000 h^{-1}. For hydrothermal stability test, the water vapor of the feed gas was provided by a glass bubbler. CH_4 conversion was analysed by an on-line gas chromatograph (Shimadzu GC-14B) equipped with an automatic sampling device and a TCD detector using a 5 A sieve column for separating CH_4, O_2 and N_2 at 55 °C. CH_4-TPR (temperature programmed reduction) measurement was performed in a conventional flow system. Samples of 50 mg each (45–60 mesh) were fixed in the middle of a quartz tubular reactor. The samples were first pre-treated in an air flow (20 ml min^{-1}) at 500 °C for 30 min, allowed to self-cool down to room temperature (RT), and then were flushed with a mixture gas of CH_4–He (4 : 96 vol%) at a flow rate of 15 ml min^{-1} for 60 min. Finally, the sample bed temperature was linearly increased from RT to 500 °C at a heating rate of 20 °C min^{-1}. CO_2 was monitored with a quadrupole mass spectrometer (Balzers QMS 200 Omnistar) as an indicator of the conversion efficiency of the oxidation reaction. The specific surface areas and micropore volumes (Table 1) of the samples were measured by nitrogen-adsorption at 77 K with a Carlo 1900 Sorptomatic instrument.

Fig. 1 compares the catalytic activities for CH_4 complete combustion over various Pd catalysts as a function of temperature. It can be seen that Pd/HZSM-5 exhibits an activity that is comparable to that of Pd/SAPO-5 prepared by the ion-exchange method,[12] and higher than that of Pd/γ-Al_2O_3 or Pd/SiO_2, indicating that the HZSM-5 support has a better enhancing effect on the activity of supported PdO species than γ-Al_2O_3 or SiO_2 supports. Moreover, the addition of Zr, Y, La and Al to Pd/HZSM-5 made modified catalysts exhibiting a considerable discrepancy in terms of activity. Compared with Pd/HZSM-5, Pd-Zr/HZSM-5 shows a remarkably higher CH_4

Table 1 Catalytic properties of Pd-supported catalysts for methane combustion (GHSV = 48000 h^{-1})

	Surface area[a]/ m^2 g^{-1}	Micropore volume[a]/ cm^3 g^{-1}	$T_{10\%}$[b]/ °C	$T_{50\%}$[b]/ °C	$T_{100\%}$[b]/ °C
Pd/HZSM-5	498.1	0.1725	317	351	415
Pd-Zr/HZSM-5	492.5	0.1702	288	333	370
Pd-La/HZSM-5	438.4	0.1578	331	387	475
Pd-Y/HZSM-5	404.0	0.1387	339	440	—
Pd-Al/HZSM-5	422.6	0.1495	335	393	520
Pd/γ-Al_2O_3	172.7[c]	0.0927[c]	352	443	490
Pd/SiO_2	197.5[c]	0.1049[c]	410	526	—

[a] Calculated from the Dubinin plot. [b] Temperatures required for 10, 50 and 100% conversion of methane, respectively. [c] Calculated from the BET plot.

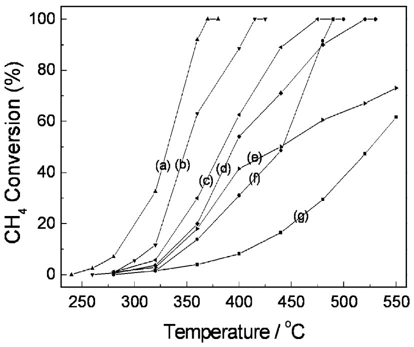

Fig. 1 Ignition curves of methane combustion over Pd-Zr/HZSM-5 (a), Pd/HZSM-5 (b), Pd-La/HZSM-5 (c), Pd-Al/HZSM-5 (d), Pd-Y/HZSM-5 (e), Pd/γ-Al_2O_3 (f), and Pd/SiO_2 (g). Feed composition: CH_4 (2%), N_2 (90%), O_2 (8%); GHSV = 48000 h^{-1}.

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† Electronic supplementary information (ESI) available: O_2-TPD and XRD patterns and interpretation of results. See http://www.rsc.org/suppdata/cc/b2/b205154k/

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ignition activity and a conversion efficiency of 100%, whereas Pd-M/HZSM-5 (M = Y, La and Al) exhibit more or less lower activities. For further comparison, the CH_4 conversion temperatures of all the catalysts are listed in Table 1. $T_{10\%}$, $T_{50\%}$ and $T_{100\%}$ represent the temperatures for 10, 50 and 100% conversions of CH_4, respectively. It can be clearly seen that Pd-Zr/HZSM-5 exhibits the best performance among all the catalysts in terms of the three conversion levels.

The thermal/hydrothermal stabilities of Pd-Zr/HZSM-5 and Pd/HZSM-5 were examined at 370 °C within 60 h. In the absence of water vapor, the CH_4 conversion efficiency (CE) over the Pd-Zr/HZSM-5 keeps as high as *ca.* 100% within 60 h, while that of Pd/HZSM-5 decreases gradually from 70% to *ca.* 45% within the initial 18 h, and thereafter the catalytic activity shows no apparent changes. In the presence of 4% water vapor, the CE over Pd-Zr/HZSM-5 decreases only from 100% to 78–82% within the initial 12 h and no further deactivation was observed. However, the CE over Pd/HZSM-5 reduces continuously to as low as 13–20% within 60 h. Moreover, the CE over Pd-Zr/HZSM-5 could be easily recovered to the initial value if increasing the reaction temperature to 390 °C or removing the 4% water vapor in the feed gas. So we can conclude that Zr-additive could greatly improve both the thermal and hydrothermal stabilities of Pd/HZSM-5. These results are critical if the Pd-Zr/HZSM-5 catalyst would be considered for practical usage in low-temperature CH_4 combustion.

CH_4-TPR was used to characterize the reactivity between PdO species and methane (Fig. 2). All the TPR curves show two major peaks. The high-temperature peak can be assigned to the syngas reaction through the CO_2 reforming mechanism occurring over reduced Pd particles. For Pd/HZSM-5, the high-temperature peak is negligible. Thus only the low-temperature peak reflects the reduction property of PdO species.[17] The low-temperature peaks could be further deconvoluted into three or more fine structures corresponding to different PdO species reacting with CH_4. The initial reduction temperatures of the samples lie between 267 and 325 °C, with Pd-Zr/HZSM-5 the lowest and Pd/SiO_2 the highest. It is also seen that the initial reduction temperature correlates very well with the ignition temperature of methane combustion reaction. This indicates that the reduction step is the rate-determining process in CH_4 oxidation catalysed by PdO species. Similar results have been reported by ourselves and others.[10,17–18]

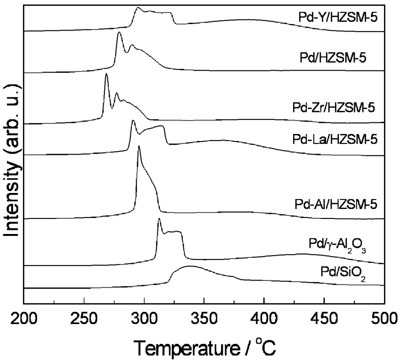

Fig. 2 CH_4-TPR profiles of the samples heated in a mixture (15 ml min^{-1}) of CH_4 (4%) and He (96%) at a heating rate of 20 °C min^{-1}.

Burch *et al.* suggested that supported PdO species play an important role in the CH_4 combustion reaction; the C–H bonds of CH_4 are activated by the $Pd^{2+}O^{2-}$ ions at the surface of the PdO by a heterolytic mechanism, and the activity on Pd increases steadily as the Pd is oxidized progressively and fully to PdO.[5,19] Thus, the readiness of PdO species being reduced by CH_4 could determine the initiating temperature of the combustion reaction. Our CH_4-TPR and O_2-TPD results show that the PdO species with the lowest desorption temperature are the most reactive ones and the Zr additive, among the ones we tested, seems to be the most effective in promoting the activity of PdO species. ZrO_2 could act as an oxygen reservoir and is also a well-known oxygen supplier, exhibiting high oxygen mobility.[8,16] Therefore, ZrO_2 could provide oxygen atoms a relatively free pathway for approaching Pd atoms. It is reasonable to assume that Pd on Pd-Zr/HZSM-5 can be easily oxidized under the reaction conditions. This leads to the C–H bonds being easily activated by $Pd^{2+}O^{2-}$ ions. Therefore, we believe that the presence of more reactive PdO species on Pd-Zr/HZSM-5 could be a main reason for its high catalytic activity for CH_4 combustion.

In summary, Zr-promoted Pd/HZSM-5 catalyst has been found to exhibit high activity, thermal and hydrothermal stabilities for low-temperature CH_4 combustion.

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