Low-temperature Complete Combustion of Methane over CeO_2-Promoted Pd/HZSM-5 Catalyst with Enhanced Activity and Stability

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High catalytic activity and thermal/hydrothermal stability in the course of the low-temperature methane combustion were characteristics of the Pd–Ce/HZSM-5 catalyst, which was easily prepared by an impregnation method.

Since methane (main constituent of natural gas) is the most difficult to oxidize among all the hydrocarbons and has a much larger greenhouse effect than carbon dioxide,[1] low-temperature complete combustion of methane is a challenging research subject in terms of energy generation and methane emission control.[2–8] In the practical applications, the catalyst must ignite reaction below 300 °C, oxidize nearly 100% of CH_4 below 400 °C, and possess a long catalytic lifetime.[4,5] The zeolite-supported Pd catalysts, such as Pd-NaZSM-5 and Pd/SAPO-5,[6–8] are known to be very active for low-temperature CH_4 combustion. However, these catalysts are typically prepared by the ion-exchange method and show significant deactivation in the coexistence of water vapor, which is a serious concern for the development of these materials for practical purposes. Consequently, considerable effort has been devoted to the development of novel catalysts with both high activity and stability. We report here on the preparation of a series of Pd/HZSM-5 catalysts without and with additives of oxides of La, Ce, Sm, Nd and Tb using an impregnation method, and the details of the activity and thermal/hydrothermal stability of catalysts.

Firstly, M/HZSM-5 ($Si/Al_2 = 165$, M = Ce, La, Sm, Nd and Tb) supports were prepared by impregnating the parent HZSM-5 powders for 12 h with aqueous solutions of the corresponding nitric salts, respectively, followed by drying at 120 °C for 12 h and calcining at 500 °C for 3 h. Then, the resulting materials were impregnated with $Pd(NO_3)_2$ aqueous solution. All Pd catalysts were obtained after repeating the above drying and calcining procedures. Except when otherwise stated, the desired loadings of all the metals in their metallic states were 1 wt% of the catalysts.

The catalytic test was performed with a fixed-bed flow microreactor at 1 atm. CH_4 conversion was analyzed with an on-line gas chromatograph (Shimadzu GC-14B) equipped with a TCD detector. CH_4-TPR measurement was performed in a conventional flow system. Samples were fixed in the middle of a quartz tubular reactor. The samples were firstly pre-treated in airflow at 500 °C for 30 min, allowed to self-cool down to room temperature (RT), and then were flushed with a mixture gas ($15\,ml\,min^{-1}$) of CH_4/He (4 : 96%) 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.

Table 1. Catalytic properties of zeolite-supported Pd catalysts for complete combustion of methane ($GHSV = 48000\,h^{-1}$)

Catalysts	Surface area /$m^2\,g^{-1}$	Micropore volume /$cm^3\,g^{-1}$	$T_{10\%}$[a]/ °C	$T_{50\%}$[a]/ °C	$T_{100\%}$[a]/ °C
Pd–HZSM-5	498.1	0.1725	317	351	415
Pd–Ce/HZSM-5	493.5	0.1710	290	336	375
Pd–La/HZSM-5	438.4	0.1578	331	387	475
Pd–Sm/HZSM-5	455.0	0.1618	326	374	430
Pd–Nd/HZSM-5	462.2	0.1643	322	371	425
Pd–Tb/HZSM-5	419.1	0.1489	329	388	540
1.23Pd/HZSM-5	—	—	310	347	405
1.23Pd/HZSM-5[b]	—	—	305	344	400

[a]Temperatures required for 10, 50, and 100% conversion of CH_4, respectively. [b]Prepared by ion-exchange method, the loading of Pd is 1.23 wt% of catalyst.

Figure 1 compares the catalytic activities for CH_4 combustion over various Pd catalysts as a function of temperature. The activity of Pd/HZSM-5 was somewhat comparable to that of Pd/SAPO-5[8] prepared by the ion-exchange method. Moreover, compared with Pd/HZSM-5, Pd–Ce/HZSM-5 showed a remarkably higher CH_4 ignition activity and a conversion efficiency of 100%, whereas Pd–M/HZSM-5 (M = La, Sm, Nd and Tb) exhibited more or less lower activities. $T_{10\%}$, $T_{50\%}$ and $T_{100\%}$, the temperatures corresponding to 10, 50 and 100% conversions of CH_4, are further compared in Table 1. One can clearly see that Pd–Ce/HZSM-5 exhibits the best performance among all the catalysts in terms of the three conversion levels. It can be also seen that two 1.23Pd/HZSM-5 catalysts, prepared by impregnation method and ion-exchange method respectively, possess closely catalytic activities. Figure 2 compares Pd–Ce/HZSM-5 and Pd/HZSM-5 for their thermal/hydrothermal stability at 370 °C within 40 h. In the presence or absence of 4% water vapor, Pd–Ce/

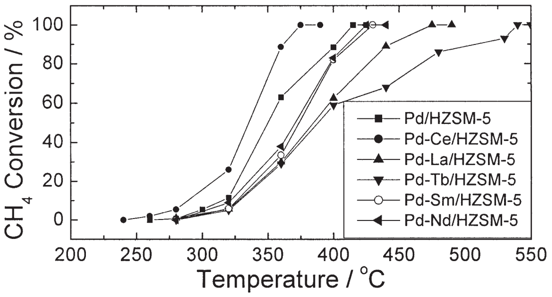

Figure 1. Ignition curves of methane combustion over Pd-supported catalysts. Feed composition: CH_4 (2%), O_2 (8%), N_2 (90%); GHSV: $48000\,h^{-1}$.

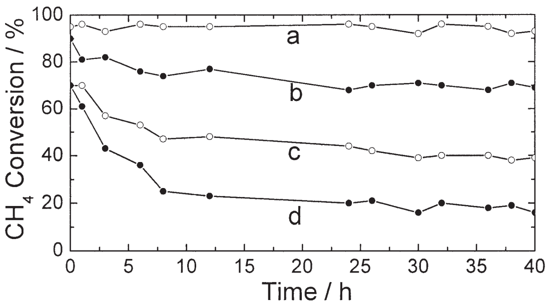

Figure 2. Time dependence of methane conversion over Pd–Ce/HZSM-5 (a, b) and Pd/HZSM-5 (c, d) in the presence and absence of 4% water vapor. Feed composition: CH_4, 2%; O_2, 8%; H_2O, 0% (○) or 4% (●); N_2, balance; GHSV: 48000 h^{-1}.

HZSM-5 showed a remarkably lower tendency to be deactivated compared to Pd/HZSM-5. Moreover, it is also worth mentioning here that the CH_4 conversion of Pd–Ce/HZSM-5 could easily be recovered to the initial value if increasing the reaction temperature to 385 °C or removing the H_2O in the feed gas.

CH_4-TPR was used to examine the reactivity between PdO species and CH_4 in the absence of free O_2 (Figure 3). All the TPR curves show two major CO_2 evolution 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 CH_4 reduction property of PdO species.[3] This shows the involvement of the PdO species of the catalyst in CH_4 combustion and also confirms that a redox mechanism occurs between PdO species and CH_4. Moreover, the low-temperature peaks could be further split into three or more fine structures corresponding to different PdO species reacting with CH_4. In combination with activity data (Figure 1), one can see that the initial reduction temperature is overwhelmingly coincident with the ignition temperature of CH_4 combustion reaction. This indicates that the initial reduction step is the rate-determining process in CH_4 oxidation catalysed by PdO species, and the PdO species with the lowest desorption temperature are the most reactive ones. Others and we ourselves have reported on similar results.[3,6]

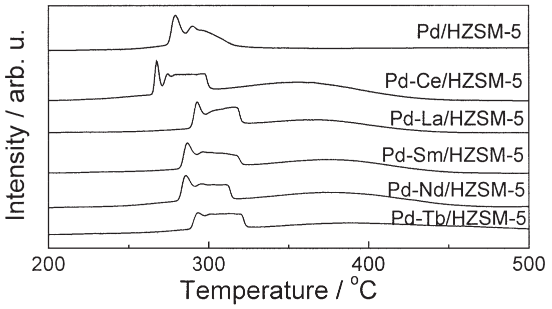

Figure 3. CH_4-TPR spectra of the samples heated in a mixture of CH_4–He (4 : 96%) at a heating rate of 20 °C min^{-1}.

It was suggested that the oxidized Pd form was considered as the most active state of the supported catalysts in CH_4 combustion reaction.[9] The weaker the Pd–O bonds, the lower is the temperature required to activate the oxygen and the higher the catalytic activity.[6] CeO_2 has the cubic fluorite structure with many oxygen vacancies, and typically possesses the high oxygen storage/supplying capacity.[10] It could provide an easy pathway for the oxygen atoms to approach or leave from the palladium particles. In this way, CeO_2 can effectively promote the reoxidation of Pd on Pd–Ce/HZSM-5 by providing oxygen, maintain the adequate oxidation state of Pd active sites under the reaction conditions, and thus promote the presence of more reactive PdO species on Pd–Ce/HZSM-5. Moreover, CeO_2 promoted reduction of PdO in a reducing atmosphere. This may be related to its withdrawing capacity of oxygen from noble metal.[11] Therefore, it is not surprising that Pd–Ce/HZSM-5 possessed weak Pd–O bonds and showed low temperatures for CH_4 oxidation, as shown by CH_4-TPR tests. On the other hand, Figure 3 also shows that La_2O_3 deteriorates reduction of PdO of Pd/HZSM-5. This could be attributed to La_2O_3's basicity.

In summary, Pd–Ce/HZSM-5 catalyst, prepared by an impregnation method, possesses remarkably enhanced thermal/hydrothermal stability and has a high potential for use as low-temperature combustion catalyst in energy generation and CH_4 emission control. The high oxygen storage/supplying capacity of CeO_2 could be the main reason leading to the presence of more reactive PdO species on Pd–Ce/HZSM-5.

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