

Catalytic conversion of methane to methanol and formic acid on singly dispersed palladium oxide species on internal surface of ZSM5

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Introduction

Methane is a relatively inexpensive energy resource [1]. The mature hydraulic fracturing technology brings supplies of this cleaning-burning energy sources from shale to global society in a safe, reliable environmental-friendly manner. It has unlocked vast energy resources located in shale and other tight rock and thus largely enhanced its availability on ground and decreased its cost. Prevision of fuel generation and consumption in 2040 made by ExxonMobil suggests the portion of CH₄ in the supply of fuels will increase by at least 10% in the next two decades [2]. One of the main applications of methane is the production of methanol. Currently, chemical industries take a two-step process: steam reforming to generate synthetic gas (CO and H₂) and a following synthesis of methanol from CO and H₂. The first step is performed at a high temperature of 600-800°C. The quite low durability of catalysts at such a high temperature is one challenging issue. In addition, the higher reaction temperature requests more input of energy. An ideal solution for utilization of CH₄ is a direct conversion of CH₄ to CH₃OH at mild condition in terms of a relatively low temperature. This has remained challenging for decades. Here we prepared ZSM5 with enchanted singly dispersed Pd₂O₄ species. It exhibits high catalytic activity and selectivity in transforming CH₄ to CH₃OH in liquid.

Materials and Methods

The Pd/ZSM5 catalysts were synthesized by incipient wetness impregnation. They were prepared by impregnation of the HZSM-5 (Si/Al = 15, Clariant) with a palladium nitrate solution (99%, Alfa Aesar) at 65°C. After impregnation, the products were dried in vacuum and calcinated in air at 450-550°C for 3h. Various nominal loadings of palladium were used. The real Pd content was determined by inductively coupled plasma optical emission spectrometry (ICP) measurements. After synthesis, Pd/ZSM5 catalysts were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS), and X-ray photoelectron spectroscopy (XPS).

Results

CH₄ is directly converted to CH₃OH on singly dispersed Pd₂O₄ species anchored on the internal wall of micro-pores of ZSM5 (0.01wt%Pd/ZSM5). The singly dispersed Pd₂O₄ species are identified with EXAFS (Figures 1 and 2 and Table 1). These sites are highly active for this direct transformation. The activity for production of organic oxygenates on 0.01wt%Pd/ZSM5 at 95°C is 16.58 molecules per Pd atom per second. The activity and selectivity of different product were listed in Figure 3a. CuO largely promotes selectivity for production of methanol from CH₄ (Figure 3b). At this temperature the selectivity for production of methanol on 0.01wt%Pd/ZSM5 with co-catalyst CuO is 98% while overall activity for organic oxygenates is 3.48 molecules per Pd per second.

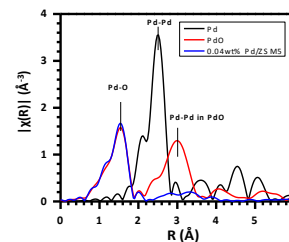


Figure 1 Fourier transform magnitudes of k²-weighted EXAFS data of 0.04wt% Pd/ZSM5 and reference systems (bulk Pd and PdO)

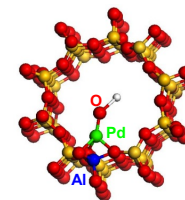


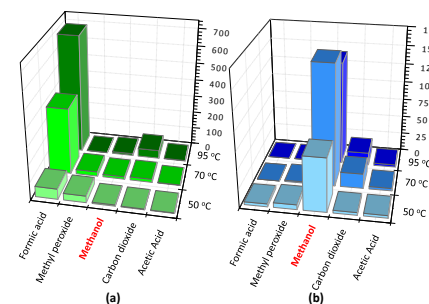
Figure 2 Structure of the Pd₂O₄ enclashed in microspores of ZSM5

Table 1. Coordination number and bond length of Pd atoms in 0.01wt%Pd/ZSM5.

Sample	N (Pd-Pd)	N (O-Pd) ^[a]	R (Pd-Pd) (Å)	R (O-Pd) (Å)
Pd foil	12	0	2.740±0.002	
0.04wt%Pd/ZSM5	0	4.12±0.49		2.001±0.009

[a] “*” marks the central atom.

Figure 3 Catalytic performance of (a) 0.01wt%Pd/ZSM5 at 50°C, 70°C, and 95°C and (b) 0.01wt%Pd/ZSM with 2wt%CuO at 50°C, 70°C, and 95°C. The amount of catalyst is 28 mg. Pressure of CH₄ is 30 bar. Oxidizing agent is 5 mmol H₂O₂ diluted in 10 ml H₂O. Reaction time is always 30 minutes upon the corresponding temperature is reached.



References

1. S. R. Golisz, T. Brent Gunnoe, W. A. Goddard, J. T. Groves, R. A. Periana, *Catalysis Letters* **2010**, *141*, 213-221.
2. Exxonmobil, **2013**, <http://corporate.exxonmobil.com/en/energy/energy-outlook>.