Role of Brønsted acid site during catalytic combustion of methane over PdO/ZSM-5: Dominant or negligible?

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ABSTRACT

ZSM-5 zeolites (NaZSM-5, HZSM-5 and Silicalite-1) with different acid nature were synthesized and used as supports of Pd catalysts for catalytic combustion of methane. Moreover, the acid property of the as-synthesized Pd/NaZSM-5 catalyst was adjusted by a NH_4^+ ion-exchange process to post-generate Brønsted acid sites and different preparation methods were investigated. The potential roles of Brønsted acid sites (anchoring Pd species or activating methane molecules) were discussed, and the experimental results indicated that the anchoring effect of Brønsted acid sites on Pd species was not directly observed. However, the acid properties of supports (the presence of Al^{3+} as Lewis acid sites, especially coordinatively unsaturated Al^{3+}) were crucial for the preparation of Pd/ZSM-5 catalysts with high Pd dispersion. Additionally, although Brønsted acid sites of ZSM-5 was contributed to the activation or even cracking of long-chain alkanes (such as *n*-decane), the direct adsorption/dissociation of methane on Brønsted acid sites was difficult and depended more on the dispersion and particle size of PdO_x. Pd/NaZSM-5 catalyst presented an outstanding durability at low-temperature (350 °C) and high-temperature (800 °C), and the high Si/Al ratio could improve the water-resistance due to its good hydrophobicity, but the reversible deactivation owing to the formation of PdO into $Pd(OH)_2$ under high concentration of water vapor was still unavoidable.

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1. Introduction

Catalytic combustion of methane has been attracted much attention for the purposes of energy utilization (such as power plants, gas turbines, house hold appliances and catalytic boilers) and air pollution abatement (for example, the emission of unburned methane from natural gas vehicles) due to methane as primary component of natural gas, which is regarded as a promising alternative to conventional thermal combustion. Catalytic combustion of methane operating at low temperature can not only obtain high energy transforming efficiency but also decrease the emission levels of noxious, which is an effective and economical strategy for the methane utilization [1,2]. Many studies have been devoted to the design of catalysts with excellent ignition activity at low temperature, however, the catalysts with high thermal stability and stable catalytic activity under the reaction conditions containing steam (5–15%) or sulphur are still urgently needed.

Over the last decades, three families of catalysts including noble-metal based catalysts (supported Pd, Pt, Rh and Au), single transition metal oxides (Co_3O_4, MnO_x, CuO and CeO_2) and mixed

metal oxides with high thermal stability (hexaaluminate, spinel and perovskite) have been investigated [2]. Among these, supported noble-metal catalysts are the most commonly studied catalysts due to their superior catalytic activity. In practice, palladium is recognized as the most active and especially the Pd/γ-Al_2O_3 catalysts (γ-Al_2O_3 displays good chemical and physical stability, high mechanical resistance and high surface area) demonstrate high activity and good thermal stability. However, an improvement of supported Pd catalysts, for instance the screening of supports, additives and preparation methods, has been always ongoing. Especially in recent years, the supports with different electrophilic/electrophobic or acid/base properties are investigated to improve the catalytic activity and stability, which can control the oxidation state or the dispersion of noble metals, and adjust the strong interactions between supports and noble metals. Zeolite, due to its high surface area, tunable acidity/basicity, excellent thermal stability and uniform/intricate channels, was considered as a good candidate. Armor reported the Pd-zeolites (Pd-ZSM-5, mordenite and ferrierite zeolites) showed much higher activities for methane combustion than that of PdO/Al_2O_3 due to the high dispersion and reducibility of Pd^{2+} [3]. Monks de Correa [4] also studied methane combustion over Pd-NaZSM-5 and Pd-NaMOR catalysts and found that the catalytic

activity was related to Na/Pd ratios and the interactions between Pd^{2+} and Na^+ was crucial to catalyze methane combustion. Niwa reported the influence of H- and Na-type ZSM-5 and MOR zeolites as a support and indicated the difference between activities of H- and Na-type zeolites was negligible, while such cations as Al^{3+} and Na^+ (Lewis acidity) suppressed the activity of palladium due to the electron withdrawing property of such cations [5]. However, the acid-base interaction between acid sites of zeolite and PdO was considered to be beneficial to the inhibition of PdO sintering [6]. Additionally, the Niwa research group found that for methane combustion on Pd/H-beta and H-ZSM-5 with different Al concentrations, the high Si/Al ratio exhibited a better performance due to the hydrophobicity of supports and the formation of agglomerated PdO [7]. Unfortunately, the acid properties of these zeolite-based catalysts were not fully characterized in these studies and the possible correlation between acidity and activity was not directly discussed, even where H-type zeolites were employed. Wang [8,9] investigated catalytic combustion of methane over Pd/ZSM-5 by pyridine-FTIR and in-situ FTIR of methane compared with that over Pd/Al_2O_3 only behaving Lewis acid sites. The experimental results showed that Brønsted acid sites were vital because the adsorption and activation of methane occurred on acidic bridging hydroxyl groups of ZSM-5. Additionally, Liu found the enhancement of the acidity of HZSM-5 treated by plasma can significantly improve the activity and stability of Pd/HZSM-5 [10]. Thereafter, Liu confirmed the bond interaction between the acidic proton and the oxygen atom of PdO (the formation of $PdOH^+$) by the DFT calculations, and acid sites in zeolite were necessary for the activation of CH_4 and keeping PdO highly dispersed [11,12].

In short, H-type ZSM-5 with sufficient Brønsted acid sites was commonly employed as a support of Pd/ZSM-5 for catalytic combustion of methane, although the parent HZSM-5 showed a poor activity. However, the role of acid sites (Brønsted and Lewis acid sites) is still not completely understood. For examples, Lou [13] and Niwa [14] considered that the highly dispersed Pd can be anchored on ZSM-5 surface through the interaction between PdO and Brønsted acid sites, while the role of Brønsted acid sites for the activation or dissociation of methane was not much discussed. Wang [8,9] proposed that Brønsted acid sites promoted the adsorption-dissociation of methane and were crucial in the catalytic combustion of methane. By comparison, the twofold roles of Brønsted acid sites were observed by Liu [11,12]. Herein, an elaborate design of catalysts was done (including the preparation of supports and post-treatment) to control precisely the acid properties of supports and catalysts, and understand comprehensively the role of acid sites in catalytic combustion of methane on Pd/ZSM-5. Firstly, H- and Na-type ZSM-5, siliceous ZSM-5 (silicalite-1) and γ-Al_2O_3 with different acid nature were prepared under similar conditions and used as supports of Pd catalysts. Meanwhile various characterizations, such as XRD, SEM, HRTEM, NH_3-TPD, CH_4-TPD, CO_2-TPD, H_2-TPR, CH_4-TPR, py-FTIR, CO-FTIR and XPS, were carried out to fully characterize acid-base, redox properties, morphology, particle size and valence state of supported palladium catalysts, and associated with catalytic activity for methane combustion. Subsequently, the different preparation methods and post-treatments were employed to determine the possible role of Brønsted acid sites in the activation of methane molecules. Moreover, the stability at low/high temperatures and the water-resistance of Pd/NaZSM-5 as a preferred catalyst were also investigated.

2. Experimental section

2.1. Catalyst preparation

The following chemicals were used in the synthesis: aluminum isopropoxide (AIP, >98%), tetraethyl orthosilicate (TEOS, >99%), polyethylene glycol 600 (PEG 600, analytical reagent), sodium chloride (NaCl, >99.5%), ammonium nitrate (NH_4NO_3, analytical reagent), sodium hydroxide (NaOH, analytical reagent), ammonium hydroxide ($\geq$28% NH_3 in H_2O), were used as received from Aladdin. Tetrapropylammonium hydroxide solution (TPAOH, 25% in H_2O) was used as received from Shanghai Cainorise Chemicals Co., Ltd., China. Palladium chloride ($PdCl_2$, 59.7 wt% Pd) was used as received from Heraeus.

2.1.1. Synthesis of NaZSM-5 and HZSM-5

NaZSM-5 was synthesized using a two-stage temperature-varied hydrothermal method under dynamic condition (60 rpm) [15]. In a typical synthesis, 0.62 g of NaCl, 5 g of PEG600, and 11.625 g of TPAOH were dissolved in 50 mL of deionized water and stirred for 15 min, and then 0.2 g of AIP was added into the mixed solutions. After ultrasound for 10 min and stirred for 15 min, 6.54 g of TEOS was added dropwise and stirred for 24 h at room temperature. The resulting colloids was transferred into a Teflon-lined stainless autoclave (100 mL). The autoclave was sealed and maintained at 80 °C for 24 h, and then 170 °C for 72 h under dynamic condition (60 rpm). The powders were collected by filtration and washed with distilled water for several times, then dried at 110 °C and calcined at 550 °C for 4 h in air flow, generating the NaZSM-5. To produce HZSM-5, the calcined NaZSM-5 samples were NH_4^+ ion exchanged four times in an aqueous solution of NH_4NO_3 (1 M, L/S = 30 mL/g) at 80 °C and calcined at 450 °C for 4 h.

2.1.2. Synthesis of SiO₂ and Al₂O₃

SiO_2 and Al_2O_3 as reference samples were prepared following the same procedures with that of NaZSM-5 without the addition of AIP or TEOS so that the influence of preparation methods were excluded as possible as we can. However, 3.0 g of AIP was used during the preparation of Al_2O_3.

2.1.3. Preparation of supported palladium catalysts

The loading of Pd was performed by a deposition precipitation method (DP). 1 mL of Na_2PdCl_4 aqueous solution (10 mg Pd/mL), not using free Pd^{2+} salts (for example, $Pd(NO_3)_2$) or H_2PdCl_4 to avoid the possible ion exchange between Pd^{2+} (H^+) and Na^+ in NaZSM-5, was added into 50 mL of deionized water to obtain the diluted Na_2PdCl_4 solution. 1 g of support (NaZSM-5, HZSM-5, SiO_2 or Al_2O_3) was ultrasonically dispersed in 150 mL of deionized water for 20 min, and then the diluted Na_2PdCl_4 solution was dropped at the rate of 1.5 mL/min by a peristaltic pump. After stirring for 2 h, the pH value of the suspensions was adjusted to 8.0 using an aqueous solution of NaOH (0.5 M), and then aged at room temperature for 4 h. The powders were collected by filtration, washed with distilled water for several times, dried at 80 °C and calcined in air at 450 °C for 4 h to obtain Pd/NaZSM-5, Pd/HZSM-5, Pd/SiO_2 or Pd/Al_2O_3 catalysts. While Pd/NaZSM-5-H was prepared by the ion exchange of the calcined Pd/NaZSM-5 in the NH_4NO_3 solution (1 M, L/S = 30 mL/g) at 80 °C. Additionally, Pd/NaZSM-5-AM and Pd/HZSM-5-AM were prepared through the aforementioned DP method using ammonium hydroxide as the precipitant; Pd/NaZSM-5-IWI and Pd/HZSM-5-IWI were fabricated by a traditional incipient-wetness impregnation (IWI) method.

2.2. Catalyst characterization

The crystal structure and phase of the samples were examined by X-ray diffraction (XRD, D/MAX 2550 VB/PC, Cu Kα radiation). The actual loading of Pd and Si/Al ratios were determined by X-ray Fluorescence (XRF) analysis on Shimadzu XRF-1800XRF. Nitrogen adsorption isotherms were obtained at 77 K using an ASAP 2460 instrument after the samples were degassed in a