

KINETIC STUDIES ON Pd/CeO₂-ZrO₂ CATALYST FOR METHANE COMBUSTION

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Summary

A 2% Pd based catalyst carried by CeO₂-ZrO₂ was prepared by solution combustion synthesis, characterized and tested for CH₄ catalytic combustion. A deep kinetic study showed that the most suitable model fitting the experimental data was the Mars van Krevelen mechanism taking into account the concentration of molecular O₂ adsorbed on the catalyst surface. The obtained activation energy values were inside the range reported in literature for similar catalysts (E_1 : 62 kJ mol⁻¹; E_2 : 75 kJ mol⁻¹; E^*_1 : 14 kJ mol⁻¹).

Keywords

Rational design of catalysts; Micro-reactors; Sustainability.

Introduction

In view of its high activity, supported PdO is usually the employed catalyst for CH₄ combustion in applications which require low auto-ignition temperatures, such as in the treatment of CNG engine exhausts, and in catalytic combustors for gas turbines. Although several studies are reported in the literature on CH₄ combustion kinetics over Pd catalysts,¹⁻⁵ there is no unanimity about the mechanisms of this reaction: Langmuir Hinshelwood (LH),^{1,2} Eley-Rideal (ER)³ and Mars van Krevelen (MvK)^{4,5} mechanisms have been proposed. In this paper a kinetic study on Pd/CeO₂-ZrO₂ is presented.

Experimental

Pd/CeO₂-ZrO₂ catalyst was prepared by solution combustion synthesis. A homogenous aqueous solution of metal nitrates as oxidizers and glycine as organic fuel, dosed in stoichiometric ratio, once dissolved in distilled water, was placed into an oven at 600 °C.⁵ Pd(NO₃)₂ was directly added to the precursors solution to co-synthesize 2% b.w. of Pd on the carrier. The as-prepared catalyst was calcined in calm air for 2 h at 750 °C and then characterized by XRD and SEM-EDS analysis; the BET specific surface area was also measured. The catalytic activity of the prepared catalyst towards CH₄ combustion was tested in a Temperature Programmed Oxidation (TPO) device. The apparatus consisted of a fixed bed reactor inserted between quartz wool (i.d. 4 mm), made of 0.05 grams of catalyst (0.4-0.6 mm) and 0.95 of SiO₂ pellets (0.3-0.7 mm). The reactor, placed in a PID-

regulated oven, was fed with 50 Nml min⁻¹ of gas (2.5% CH₄; 7.5% O₂; He to balance). The temperature was increased up to 850 °C (50 °C min⁻¹). During the oven cooling, the CH₄ concentration was measured every 10 °C with a NDIR analyzer (Hartman and Braun URAS 10E). The half-conversion temperature (T_{50}) was regarded as an index of the catalytic activity.

A reaction kinetics study was performed to establish the more appropriate kinetics law and the temperature dependence of the characteristic kinetic parameters. The experimental test rig was based on a continuous recycle microreactor, employing the above described quartz tube for the catalyst housing. The amount of pelletized catalyst was 0.5 g, diluted with 0.45 g of SiO₂. The recycle was enabled by a Teflon-membrane pump. Analysis of the inlet and outlet gas feeds were performed via the above described analytical tools. The feed flow rate was kept equal to 50 Nml min⁻¹, whereas the overall recycle flow rate passing through the reactor was 1,050 Nml min⁻¹. This was sufficient to eliminate almost any external mass transfer effect on the overall conversion measured. In such conditions, the maximum CH₄ concentration variation throughout the catalyst packed-bed was about 10%. Within these limits the average values of O₂ and CH₄ partial pressure in the catalyst were assumed as reference data for the assessment of a kinetic law. Besides, assuming a tortuosity factor equal to 2 for the catalyst pellets, also the internal mass transfer did not significantly affect the attained conversion (effectiveness factor always higher than 0.999). Runs were performed in the temperature

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range 380-580 °C and the absolute operating pressure was practically equal to 1 bar. The O₂ and CH₄ feed concentrations in He were varied in the ranges 2-15% and 0.5-2.5%, respectively.

Results and discussion

The XRD diffraction patterns of the as-prepared catalytic powders showed that the obtained catalyst presented a good crystalline degree, with very well detectable peaks. No diffraction peaks related to Pd were detectable, a sign that Pd dispersion was satisfactory. The BET value of the catalyst was 74.6 m² g⁻¹. The SEM analysis showed a spongy structure, with nanometric porosity. The T₅₀ value from the TPO analysis was equal to 420 °C.

The present kinetic study was based on the steady-state CH₄ reaction rate (R_{CH₄} in mol_{CH₄} s⁻¹ g⁻¹) data, operating the reactor under a differential regime of CH₄ conversion (< 0.15). R_{CH₄} was calculated according to:

$$R_{CH_4} = \frac{F_{fed} \cdot \Delta_{CH_4}}{M_{cat}}$$

where F_{fed} is the flow rate fed to the differential reactor, Δ_{CH₄} is the reacted CH₄ and M_{cat} the catalyst mass loaded into the reactor. The absence of mass transfer limitations at the reaction conditions was verified both experimentally and theoretically. The external diffusion mass transfer resistance was evaluated theoretically and found negligible.

Mars van Krevelen (MvK) models are the most frequently used to describe the oxidation of organic compounds over noble metals as well as over many metal oxides. Among noble metals, MvK mechanisms are likely to occur for Pd and Rh, since it was observed that they present different interchangeable catalytically active oxidation states at the reaction conditions used for HCs oxidation.⁵ The best kinetics law for data fitting was the MvK mechanism taking into account the concentration of molecular O₂ adsorbed on the catalyst surface:⁵

$$R_{CH_4} = \frac{k_1 k_2 \cdot p_{CH_4} p_{O_2}}{k_2 p_{CH_4} + k_1 p_{O_2}} \cdot \left(1 - \frac{k_1 p_{O_2}}{k'_1} \right)$$

$$k_i = k_i^\infty \cdot \exp\left(-\frac{E_i}{RT}\right)$$

where k₁ [mol g⁻¹ s⁻¹ bar⁻¹] is the rate constant for the molecular O₂ adsorption, k₂ [mol g⁻¹ s⁻¹ bar⁻¹] is the rate constant for the reaction between CH₄ and adsorbed molecular O₂ and k'₁ [mol g⁻¹ s⁻¹] is the rate constant for adsorbed molecular O₂ dissociation. The reaction kinetics constants k₁, k₂ and k'₁ can be expressed as a function of T by Arrhenius equation. Table 1 lists all the values of the

kinetics parameters derived by least-squares fitting of the experimental data. Other considered kinetics mechanisms (other MvK, LH, ER) led in this specific case to thermodynamically inconsistent adsorption heats and activation energies, or negative kinetic parameters.

Table 1: Kinetic values determined for 2% Pd/CeO₂-ZrO₂ catalyst.

E ₁	62 kJ mol ⁻¹
E ₂	75 kJ mol ⁻¹
E' ₁	14 kJ mol ⁻¹
k ₁ [∞]	36.74 mol g ⁻¹ s ⁻¹ bar ⁻¹
k ₂ [∞]	158.6 mol g ⁻¹ s ⁻¹ bar ⁻¹
k' ₁ [∞]	6.54·10 ⁻³ mol g ⁻¹ s ⁻¹ bar ⁻¹

Conclusions

A 2% Pd based catalyst carried by CeO₂-ZrO₂ was prepared by solution combustion synthesis, characterized and tested for CH₄ catalytic combustion. A deep kinetic study showed that the most suitable model fitting the experimental data was the Mars van Krevelen mechanism taking into account the concentration of molecular O₂ adsorbed on the catalyst surface. The obtained activation energy values were inside the range reported in literature for similar catalysts.

References

- (1) Groppi, G. Combustion of CH₄ over a PdO/ZrO₂ catalyst: an example of kinetic study under severe conditions. *Catalysis Today* **2003**, *77*, 335.
- (2) Tseng, T.-K.; Chu, H.; Ko, T.-H.; Chaung, L.-K. The kinetic of the catalytic decomposition of methyl isobutyl ketone over a Pt/γ-Al₂O₃ catalyst. *Chemosphere* **2005**, *61*, 469.
- (3) Seimanides, S.; Stoukides, M. Solid electrolyte aided study of methane. oxidation on palladium. *Journal of Catalysis* **1986**, *98*, 540.
- (4) Garbowski, E.; Feumi-Jantou, C., Mouaddib, N.; Primet, M. Catalytic combustion of methane over palladium supported on alumina catalysts: Evidence for reconstruction of particles. *Applied Catalysis A: General* **1994**, *109*, 277.
- (5) Hurtado, P.; Orodomez, S.; Sastre, H.; Diez, F. V. Development of a kinetic model for the oxidation of methane over Pd/Al₂O₃ at dry and wet conditions. *Applied Catalysis B: Environmental* **2004**, *51*, 229.