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Original Research

Catalytic Properties of Ag/SnO_2 Catalysts Applied in Low-Temperature Methane Oxidation

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Abstract

This paper focuses on the catalytic properties of Ag/SnO_2 for low-temperature methane oxidation. The influences of the metal loading (0.2-20 wt.% Ag), support (Al_2O_3, TiO_2, SiO_2) and methane concentration (0.375-1.5%) in the oxidized mixture were investigated. It was observed that the optimal amount of silver in Ag/SnO_2 was 1 wt.%. Lower or higher amounts cause a loss in catalytic activity. SnO_2 was found to be undoubtedly the best support for the title reaction among all tested oxides. A mechanism of methane oxidation over Ag/SnO_2 was proposed.

Keywords: total methane oxidation, Ag catalysts, tin oxide

Introduction

Methane is the second largest contributor to global warming after carbon dioxide. Its participation in total greenhouse gas emissions is estimated at 19%, while CO_2 emission is estimated at 50%. Worth notice is the fact that, in spite of lower emissions, methane is much more potent than carbon dioxide in terms of the greenhouse gas impact. Its global warming potential (GWP, a measure of how much a given mass of greenhouse gas contributes to global warming) is evaluated at 23, while GWP of CO_2 is 1.

According to the overall oxidation reaction (1), 1 kg of CH_4 produces 2.75 kg of CO_2. That is, when 1 kg of CH_4 is mitigated, 20.25 kg of CO_2 emission is reduced in terms of the global warming impact [1].

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O,\ \Delta H = -802.7\ \text{kJ/mol} \quad (1)$$

Methane is emitted from a variety of both human-related (anthropogenic) and natural sources. Natural sources of methane include wetlands, gas hydrates, permafrost, termites and oceans. Human-related activities include fossil fuel production, biomass burning, animal, rice cultivation, coal mining and waste management. These activities release significant quantities of methane to the atmosphere. It is estimated that 60% of global methane emissions are related to anthropogenic sources.

It has to be mentioned that methane is an important source of energy. That is why efforts to prevent or utilize methane emissions can provide significant energy, economic and environmental benefits. That is possible only when methane concentrations overcome 40%.

Lower concentrations (about 30%) can be mitigated by burning. However, the process requires temperatures over 1000^{o}C.

Hence, serious concern is methane emission from coal mine, and pigsty ventilation air or natural gas-fuelled (NGV) vehicles. That is because methane concentrations in mentioned emissions are low (to 1%). Too low to be utilized or easily mitigated.

That is why the catalytic combustion of methane seems to be a promising method for preventing methane emissions.

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A good catalyst for low-temperature methane oxidation must be active under inconvenient conditions such as low temperatures (less than 500-550ºC), low concentrations of methane (to 1%), large excess of oxygen, large amounts of water vapour and CO_2 and in the presence of poisons such as SO_x, H_2S, NO_x, HCl and NH_3

So far, the most promising are catalysts supported by SnO_2, especially palladium catalysts [2-4].

This paper is focused on silver catalysts supported by SnO_2, as we believe Ag/SnO_2 may have excellent performance in methane oxidation.

The aim of this paper is to investigate the catalytic properties of silver catalysts supported by SnO_2 in the complete methane oxidation. The results have provided the basis for probable mechanisms of the title reaction.

Experimental

Samples Preparation

Silver was loaded by impregnation with an aqueous solution of $AgNO_3$. Five supports were used. Four of them were commercial powders:

- SnO_2 (Aldrich Chemical Comopany)
- SnO_2 prepared by dissolving metallic Sn in HNO_3, drying at 200°C and calcinated at 600°C
- Al_2O_3 (Fluka)
- TiO_2 (Degussa)
- SiO_2 (Merck)

After evaporating the water, the samples were dried at 200°C for 2h and calcinated at 450°C for 2h in air.

To examine the effects of a support on catalytic activity, the loading of silver was 1 wt.% of the catalysts. 0.2-20 wt.% Ag samples were used in order to examine influence of silver concentration on catalytic activity of Ag/SnO_2 (Aldrich) in the reaction.

1 wt.% Ag/SnO_2 (Aldrich) sample was used to examine the effect of methane concentration in oxidized gas mixture on catalytic performance.

Table 1. BET surface area of supports and Ag/SnO_2(Sn) catalysts.

	$S_{BET,}$ m^2/g
SnO_2 (Aldrich)	5.16
TiO_2 (Degussa)	25
Al_2O_3 (Fluka)	120.5
SiO_2 (Merck)	231
SnO_2 (Sn)	7.12
1 wt.%Ag/SnO_2 (Sn)	7.29
5 wt.%Ag/SnO_2 (Sn)	8.91
10 wt.%Ag/SnO_2 (Sn)	7.71

Specific surface area of catalysts was determined by BET method using nitrogen adsorption. Chosen BET surfaces are given in Table 1.

Catalytic Oxidation of Methane

The measurements of catalytic activity were carried out by Temperature Programmed Surface Reaction in the temperature range 25-500°C. A constant gas flow rate 40 cm^3/min and controlled linear temperature growth of 20°/min were applied. In each experiment 0.2g of catalyst was used. The changes of CO_2 concentration were monitored by Infrared Gas Analyzer (IR Fuji Electric Co.). Catalytic activity was characterized by temperatures of 40% and 80% conversion (T_{40} and T_{80}).

Results and Discussion

Effect of Silver Concentration

Fig. 1 presents how silver concentration affects catalytic activity of Ag/SnO_2. It can be observed, that there is an optimal metal loading. Fig. 2 presents changes of T_{80} vs. silver concentration. We can state that 1 wt.% Ag/SnO_2 was found to be most active in comparison to other tested catalysts. Lower and higher amounts lead to significant loss in catalytic activity.

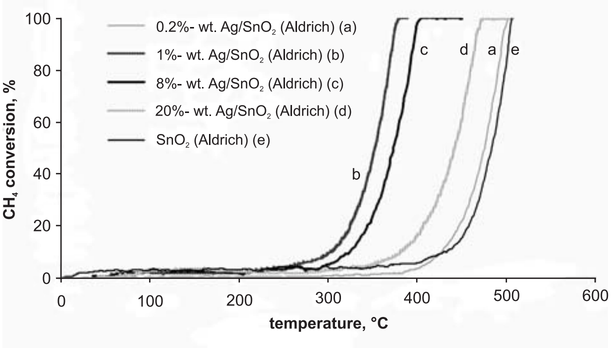

Fig. 1. The catalytic activity of Ag/SnO_2 (Aldrich) in CH_4 oxidation to CO_2.

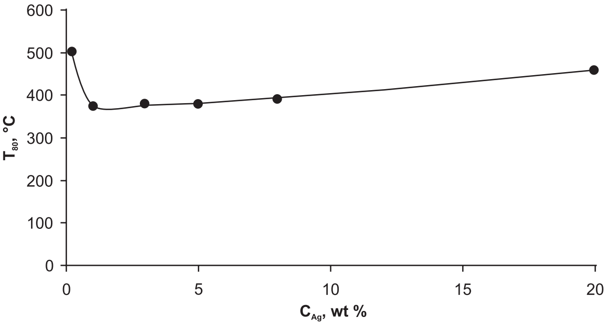

Fig. 2. The influence of silver concentration on CH_4 80% conversion for Ag/SnO_2 (Aldrich).

Effect of a Support

Fig. 3. presents conversion of methane vs. temperature over 1 wt.% Ag supported by different oxides (Al_2O_3, TiO_2, SiO_2). Overall catalytic activity was characterized by temperatures T_{40} and T_{80}, which are summarized in Table 2.

1 wt.% Ag/SnO_2 was found to have excellent catalytic performance and the reaction occurs at significantly lower temperature. Pt/SnO_2 shows similar activity. We can state that BET surface does not affect catalytic activity. The performance of catalysts with bigger BET surface than SnO_2 was far worse. We assumed that catalytic activity of Ag/SnO_2 is determined by properties of SnO_2 surface.

Effect of Methane Concentration

In order to investigate the influence of methane concentration on catalytic performance, four gas mixtures (methane + air) were used. Catalytic activity of 1 wt.% Ag/SnO_2(Aldrich) was investigated. It was found that the higher methane concentration in gas mixture results in an increase in the reaction rate and catalytic activity. Results are presented in Fig. 4.

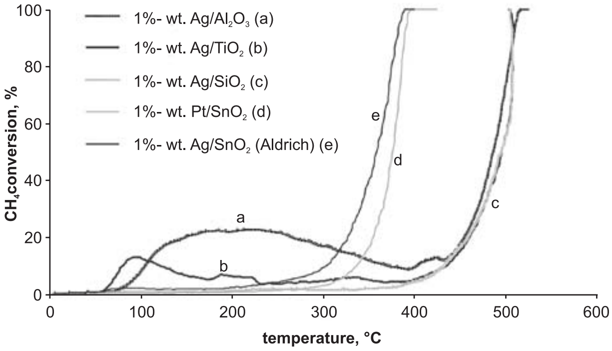

Fig. 3. The catalytic activity of silver catalysts in CH_4 oxidation to CO_2.

Table 2. 40% and 80% CH_4 conversion temperature for silver catalysts.

Catalyst	T_{40}, °C	T_{80}, °C
1 wt.% Ag/SnO_2 (Aldrich)	352	375
1 wt.% Pt/SnO_2 (Aldrich)	372	386
1 wt.% Ag/$Al._2O_3$	466	492
1 wt.% Ag/TiO_2	488	507
1 wt.% Ag/SiO_2	486	507

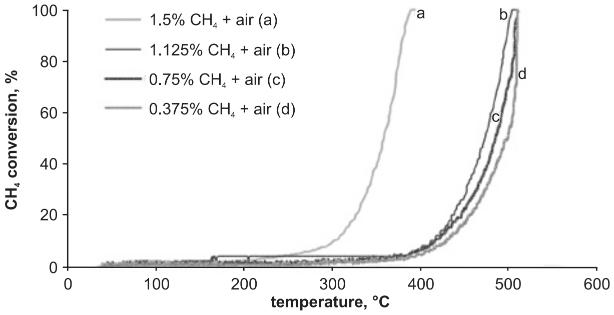

Fig. 4. The influence of CH_4 concentrations on catalytic activity of 1 wt.% Ag/SnO_2 in methane oxidation.

Reaction Mechanism

To explain why tin oxide appears to be the best support for methane oxidation catalysts, it is essential to examine SnO_2 nature. Tin dioxide as an n-type semiconductor has in its structure oxygen vacancies [5]. The oxygen vacancies are active centres on which oxygen can be adsorbed. Fig. 5. presents SnO_2 structure [6].

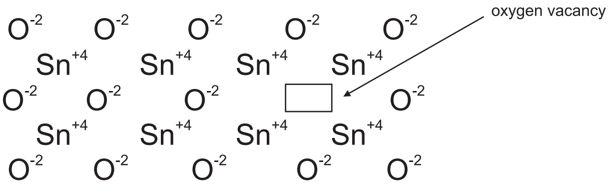

Fig.5. SnO_2 structure [6].

Equations (2) and (3) describe oxygen adsorption and vacancy formation.

$$2Oo^x + 4Sn_{Sn}^{x} \leftrightarrow O_2\uparrow + 2Vo^{\cdot\cdot} + 4Sn_{Sn}' \qquad (2)$$

$$O_2(g) + 2Vo^{\cdot\cdot} + 4e \leftrightarrow 2Oo^x \qquad (3)$$

where $Vo^{\cdot\cdot}$ – double ionized oxygen vacancy
Oo^x – oxygen anion in normal lattice position
Sn_{Sn}^{x} – tin cation in normal lattice position
$O_{2(g)}$ – oxygen in gaseous state

Oxygen adsorbed on the surface may have several forms, dependant on temperature [7].

$$O_{2(ads)} \xrightarrow{+e} O^-_{2\,(ads)} \xrightarrow{+e} 2\,O^-_{(ads)} \xrightarrow{+2e} 2O^{2-}_{(lattice)} \qquad (4)$$

Complete methane oxidation is described by reaction (5):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (5)$$

The equation is preceded with the following indirect reactions:

$$CH_4(ads) + O(surf) \leftrightarrow CH_3OH \qquad (6)$$

$$\mathrm{CH_4(ads) \leftrightarrow CH_3(ads) + H(ads)} \qquad (7)$$

$$\mathrm{2CH_3(ads) \leftrightarrow C_2H_4 + 2\ H(ads)} \qquad (8)$$

$$\mathrm{2CH_3(ads) + O(surf) \leftrightarrow CH_3CH_2O\ (ads) + H(ads)} \qquad (9)$$

$$\mathrm{CH_3(ads) + 2O(surf) \leftrightarrow HCOO(ads) + 2\ H(ads)} \qquad (10)$$

$$\mathrm{2\ H(ads) + Oo^{x} \rightarrow H_2O + Vo^{\cdot\cdot}} \qquad (11)$$

$$\mathrm{Vo^{\cdot\cdot} + 2O_2 + ne \leftrightarrow 2Oo^{x}} \qquad (12)$$

In reaction (11) and (12) additional oxygen vacancies are formed as a result of the presence of hydrogen. That means that the number of active centers on which oxygen can be chemisorbed increases.

On the basis of research we can now propose a methane oxidation mechanism.

In cases of methane oxidation over SnO_2 we assume that methane reacts with very active oxygen (O^-) adsorbed on a tin oxide surface (Fig. 6) [8-10]. Because O^- concentration is restricted to 1% of SnO_2 monolayer (Weisz limitation) [11], hydrogen from CH_4 reacts with oxygen from SnO_2 lattice.

In the case of methane oxidation over Ag/SnO_2 catalyst, in the first stage methane reacts with oxygen-forming CH_3–O. In next stage CH_3 – O molecule reacts with Ag_2O (14), resulting in Ag_2O reduction. After a while, in atmosphere of gaseous oxygen silver is reoxidated (15).

The postulated mechanism (Fig. 7) is described by reactions (13-15):

$$\mathrm{CH_4 + O^-_{ads} \rightarrow (CH_3 - O -)_{ads} + H_{ads}} \qquad (13)$$

$$\mathrm{Ag_2O + (CH_3 - O\ \text{-})_{ads} \rightarrow Ag + [\ CO_2 + H_2O\ ]} \qquad (14)$$

$$\mathrm{Ag + 1/2\ O_2 \rightarrow Ag_2O} \qquad (15)$$

The postulated reaction mechanism explains the good catalytic performance of Ag/SnO_2 in comparison to e.g. Ag/TiO_2. Despite the fact that TiO_2 is an n – type semiconductor having in its structure oxygen vacancies and similar electric properties, the oxide does not adsorb oxygen on the surface, resulting in lack of active oxygen forms (O^-) [12].

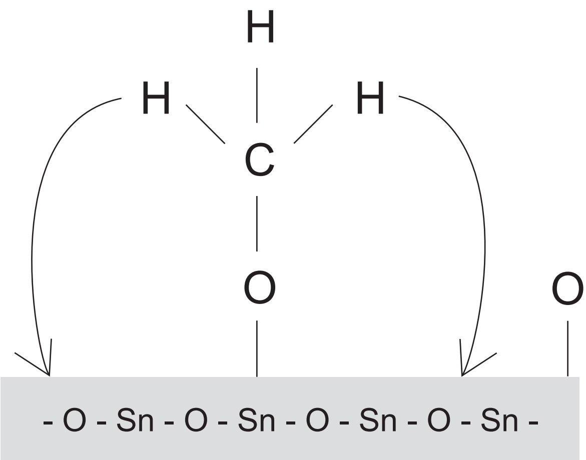

Fig. 6. The postulated mechanism of methane oxidation over SnO_2.

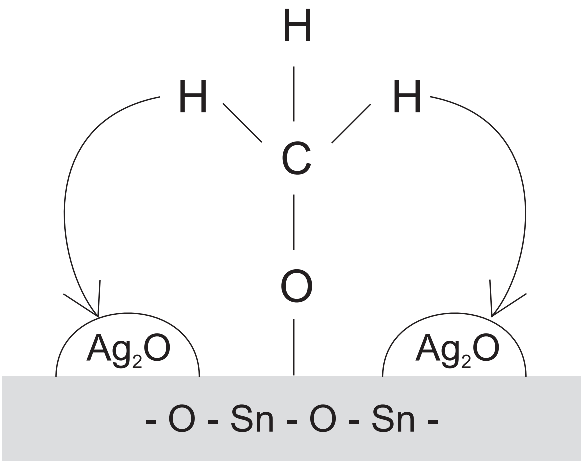

Fig. 7. The postulated mechanism of methane oxidation over Ag/SnO_2.

The mechanism confirms the results of influence of methane concentration on catalytic activity. The higher methane concentration in oxidized mixture, the more hydrogen molecules that may react with surface oxygen, contributing to higher reaction rate and better activity.

Conclusions

Taking into account the research results of catalytic methane oxidation over Ag/SnO_2 described above, the following conclusions can be made:

1. SnO_2 was found to be excellent support for silver catalysts for methane oxidation
2. The catalytic activity of Ag/SnO_2 significantly depends on:
   - concentration of metallic phase
   - concentration of methane in oxidized mixture
3. The results provide the basis for mechanisms which establishes participation of both SnO_2 and silver in the reaction (synergistic effect).

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