Method for preventing air pollution: Methane oxidation by two types of catalysts

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Abstract   Methane oxidation using different catalysts is an useful process for preventing air pollution. This study presents the methane oxidation by two types of catalysts: $Pd-Sn/Al_2O_3$ and spinel mixed oxide, $CuFe_2O_4$. The $Pd-Sn/Al_2O_3$ was successfully prepared by sol-gel method and $CuFe_2O_4$ by co-precipitation method. The catalysts obtained have been characterized structurally, morphologically and texturally by X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area (BET). The catalytic activity tests regarding methane oxidation were also performed.

Keywords: bimetallic material, copper ferrite, mixed oxides, catalytic activity tests

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1. Introduction

Catalytic combustion of methane represents an efficient process for controlling air pollution. For heat generating processes, catalytic combustion advantage consists in their ability to completely oxidize combustible poor mixtures, causing a sharp decrease in the reaction temperature of the system [1-2].

Methane, the main component of natural gas, is economical, clean but difficult to oxidize. Highly active catalysts are required to initiate the catalytic combustion of methane at low temperature [3-4].

 Methane sources are diverse such as: swampy areas, gaseous hydrates from the ocean floor, permafrost, oceans, freshwater organisms, organic deposits, landfills, oil systems, active mines, abandoned mines, paddy etc.

Methane is the most important greenhouse gas after carbon dioxide (CO_2). Its concentration in the atmosphere is relatively low, but methane is 20 times more effective than carbon dioxide gas in the capture of solar heat [5-6]. Other significant greenhouse gases are nitrous oxide and halogenated hydrocarbons [7]. These gases are generated by both natural sources and industrial activity [8]. Important methane pollution sources come from landfills, livestock farming, as well as production, transportation and use of fossil fuels.

Methane concentrations increased rapidly with industrialization that followed World War II, then followed a period of relative stability in the 90s, and nowadays it was registered a new growth [5-6].

After the new calculations, the effect of methane on global climate warming could double as originally considered. The new interpretation reveal that methane emissions had a great share in global warming of greenhouse gases between 1975 and present [9-10].

The purpose of this study was to investigate and compare the potential of using as catalysts for methane oxidation of two materials: $Pd-Sn/Al_2O_3$ and $CuFe_2O_4$.

2. Experimental

2.1. Catalysts preparation

The catalytic support was obtained by sol-gel method in the presence of a template agent (stearic

acid). The $Al(OC_3H_7)_3$: $C_{18}H_{36}O_2$: C_3H_7OH molar ratio was 1: 0,2: 30. The aluminium precursor and water molar ratio was 1: 3. The reaction mixture was kept under reflux at 80^0C for 100h, until a white precipitate was formed. The precursor was washed several times with alcohol, filtered and dried in air. After that, it was calcinated at 600^0C for two hours. The bimetallic material was prepared by sol-gel method using the $PdCl_2$ and $SnCl_2$ in ethylene glycol solution brought to pH 11 by addition of ammonia. The composition for the Pd–Sn consists of 1 wt% of noble metal and 1 wt% of Sn. The value of pH was chosen to ensure the cationic exchange between the precursor salt and the support. The mixture was stirred for 12 h, under reflux and then ammonia and ethylene glycol were evaporated by heating on a sand bath. Finally, after drying overnight at 90^0C, the material was calcinated at 200^0C for 1h. The obtained $Pd-Sn/Al_2O_3$ material was analyzed by X-ray diffraction and scanning electron microscopy (SEM). Also BET (Brunauer–Emmett–Teller) surface was investigated.

$CuFe_2O_4$ was obtained by co-precipitation method, starting from $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 2H_2O$, using a 2:1 molar ratio. The pH 12 was obtained by adding KOH as precipitation agent. The reaction mixture was kept under reflux at 80^0C for 2h, until a black precipitate was formed. After the purification process which implies washing several times with water and ethanol (10:1), the precursor was calcinated at 400^0C for 2h in order to obtain a single phase $CuFe_2O_4$ powder. $CuFe_2O_4$ powder was characterized by SEM analysis. More details regarding the synthesis and characterization of $CuFe_2O_4$ were presented in other research paper [11]

2.2. Catalytic activity measurements

Catalytic combustions of methane on the two investigated materials were carried out at atmospheric pressure in a fixed-bed quartz tubular reactor with an inner diameter of 10 mm. The reactor was placed inside an electric oven equipped with an automatic temperature controller. Catalyst loading used was 30-90mg. The experiments were done in the 200-500⁰C temperature range for Pd-Sn/Al_2O_3 and 200-400⁰C for $CuFe_2O_4$ respectively. The material wrapped in fiberglass layers was placed in the middle of the reactor, and a thermocouple was

inserted near the outlet of the material. Prior to the reaction, the material was activated under air flow at 450 °C for 1 h. After bringing the catalyst bed at 200°C, a reactant mixture consisting of methane (10 vol.-%), O_2 (12 vol.-%) and balanced with nitrogen and argon was fed to the reactor by bubbling air at a rate of 15 ml/min and N_2 at a rate of 5 ml/min through a saturator containing methane at 0°C, resulting in a gas hourly space velocity (GHSV) of 10000 h^{-1} based on the total material volume and an oxygen/methane molar ratio of 12/10 in the feed gas. Afterwards, the material bed was heated to 500°C with a heating rate of 2.5°C/min and during the reaction, the exit gases were periodically sampled and analyzed using an online gas chromatograph (GC) equipped with a SE-30 column. The temperature ramp of 2.5 °C/min was considered to be sufficiently slow to reach a pseudo-steady state at every point. The sample was injected into a gas chromatograph (GC) and the CO_2, CO, O_2, CH_4, concentrations were determined by using a thermal conductivity detector (TCD) and integrator. The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppm and the upper percent range. For CO_2, CO, O_2 and CH_4, the sensitivity limit is in the low ppm range.

The conversion of methane was calculated as a function of the reaction temperature from the amount of methane at the inlet and outlet of the reactor.

$$conversion = \frac{CH_4 in - CH_4 out}{CH_4 in} \cdot 100 \qquad (1)$$

3. Results and Discussions

3.1. XRD analysis

The $Pd-Sn/Al_2O_3$ powder obtained has cubic structure (Fig.1). X-ray diffraction analysis reveals new peaks characteristic of our Pd-Sn bimetallic particles and characteristic peaks for Al_2O_3. The average crystallite size was calculated with the formula of Scherrer and is 40nm. The JCPDS 10-0425 is assigned to γ- Al_2O_3 and JCPDS 03–065–2603 corresponds to Pd-Sn.
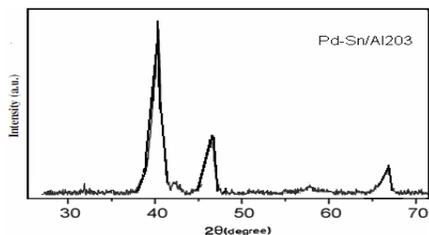
Fig.1. XRD patern of Pd-Sn/Al$_2$O$_3$, calcined at 200^{0}C/1h

3.2.SEM analysis

The morphology of Pd-Sn/Al$_2$O$_3$ and CuFe$_2$O$_4$ powders, obtained by calcination at 200^{0}C/1h and 400^{0}C/2h respectively, were evaluated by scanning electron microscopy (SEM) and were illustrated in **Fig.2** and **Fig.3**.
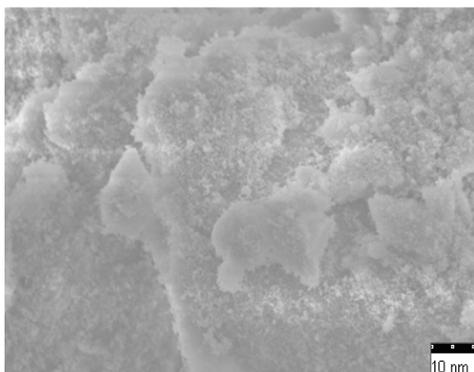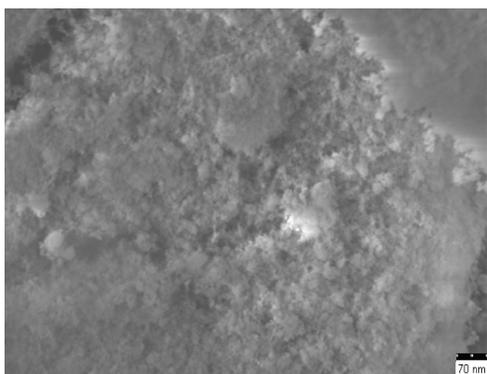

Fig.2. SEM image of Pd-Sn/Al$_2$O$_3$

Fig.3.SEM image of CuFe$_2$O$_4$

A higher tendency of the particles to form agglomerates it was observed in the case of CuFe$_2$O$_4$ (Fig.3). Both samples present spherical shape particles. The average particles size is 10nm for Pd-Sn/Al$_2$O$_3$ and 70nm for the CuFe$_2$O$_4$ and the average aglomerates size is 50 nm for Pd-Sn/Al$_2$O$_3$ and 90 nm for the CuFe$_2$O$_4$.

3.3. Specific surface area and BJH adsorption/desorption analyses

The *BET* surface area for the Pd-Sn/Al$_2$O$_3$ is 211m²/g (**Fig.4**). The BJH adsorption cumulative surface area of pores is 20m²/g and BJH desorption cumulative surface area of pores is 21m²/g (**Fig.5**). The BJH is the method of Barret, Joyner and Halenda for the pores distribution investigation.
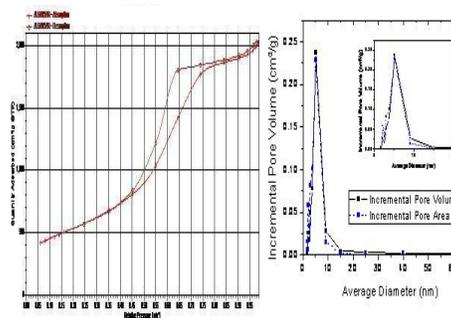

Fig.4. Adsorption isotherm for Pd-Sn/Al$_2$O$_3$

Fig.5. BJH adsorption dV/Dd pore volume for Pd-Sn/Al$_2$O$_3$

The *BET* surface area for the CuFe$_2$O$_4$ is 9,15m²/g. The BJH adsorption cumulative surface area of pores is 10m²/g and BJH desorption cumulative surface area of pores is 9,05m²/g [11].

3.4. Methane conversion

The curves of methane conversion versus the reaction temperature for the two samples are shown on **Fig.6**. At the beginning of the reaction, the catalytic activity increases very slowly, followed by a sharp increase and then a slow increase in the catalytic activity once again.
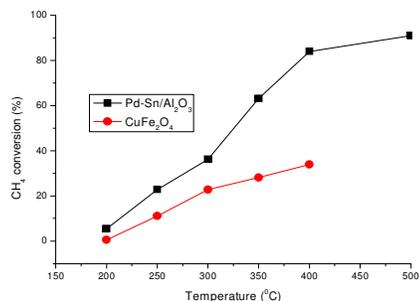
Fig.6. The methane conversion versus temperature for the Pd-Sn/Al$_2$O$_3$ and CuFe$_2$O$_4$ materials

3.5. The kinetics study of methane oxidation reactions

Activation energies were evaluated using the Arrhenius representations of rate constant dependence according to the inverse of temperature (**Fig.7**). From the slope were calculated activation energies.

In the case of these two investigated materials, it was obtained a linear dependency of ln k versus 1/T. Activation energy values for the two investigated materials are in the range 118-203KJ/mol.
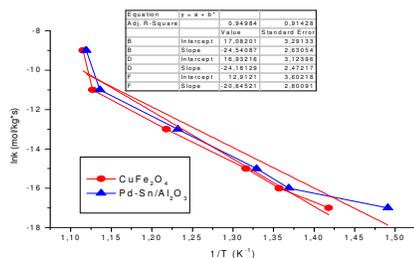

Fig.7. Arrhenius representation: the constant rate variation versus temperature for Pd-Sn/Al$_2$O$_3$ and CuFe$_2$O$_4$

As it can be seen from the graph, as the temperature increases, the constant rate decreases. Two correlation factors (R^2) satisfactory were obtained for the materials investigation between 0.945 and 0.949 respectively.

4. Conclusion

The low activation energy and high reaction rates reflected in high methane conversions. The best results for the methane conversion were obtained for the Pd-Sn/Al$_2$O$_3$, with up to 87% methane conversion. CuFe$_2$O$_4$ material presented 33% methane conversion. Lower conversions (up to 33%) were obtained with the CuFe$_2$O$_4$ material. Also, it was observed that methane conversion increases with increasing temperature.

5. References

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