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ScienceDirect
Mining Science and Technology 20 (2010) 0913–0916
MINING SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/jcumt

Improving anti-sulfur performance of methane sensors by new vectors and active components

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Abstract: Conventional Pd/γ-Al_2O_3 methane sensors are easily poisoned in a sulfur-containing atmosphere, with a subsequent decrease in sensitivity and the working life of methane sensors. We mainly investigated the effect of nanotechnology and a cerium co-catalyst on the stability and anti-sulfur performance of methane sensors. In our experiment, an anti-sulfur methane sensor was prepared by immersing cerium-containing γ-alumina nanometer elements into a Pt-Pd bimetallic nanometer catalyst. The experiment about the sensitivity and stability performance of different catalytic methane sensors indicate that sensitivity, decreased by catalyst sulfur poisoning, is improved significantly by adding cerium to the vector. As well, the long-term operational stability of methane sensors increased significantly.

Keywords: Cerium; anti-sulfur; stability; sensitivity

1 Introduction

Methane is one of the major risks in coal mines and its detection is one of the more effective measures to prevent gas explosions. So far, a catalytic combustion type of gas sensor is one of the most conventional methane sensors in the world. Generally, its catalytic element is obtained by coating vector of Al_2O_3 with spiral platinum wire, Pt-Pd and other transition metal oxides are also used as catalyst[1].

Because sulfide gases such as H_2S, SO_2 etc. are always found in methane gas in coal mines, it is easy to have the following reactions with metal catalysts or metallic oxides as shown in (1). Pt, Pd sulfide and other complex sulphides are generated and result in sulfur poisoning over the catalyst and thus decrease the sensitivity and stability of catalytic elements[2]. Simultaneously, the sulfur poisoning over the catalyst speeds up carbon deposition on the surface of the catalyst, therefore affecting the activity of the catalyst[3].

$$\begin{cases} H_2S + PtO \xrightarrow{HT} PtS,\ PtS_2,\ Pt_2S... \\ H_2S + PdO \xrightarrow{HT} PdS,\ PdS_2,\ Pd_2S... \end{cases} \quad (1)$$

In recent years, with thorough investigations of catalytic material, more attention is paid to the improvement of some special co-catalysts such as CeO_2, La_2O_3, BaO in catalytic combustion. Catalytic performance can be enhanced significantly by doping these co-catalysts with a pure alumina vector. In this way, these multi-component vectors help to stabilize specific surface areas and improve their anti-sulfur ability significantly[4-5]. Some studies have focused on nanotechnology, used in the preparation of vectors and co-catalysts, with successful results. We prepared methane nanometer sensors, tested the anti-sulfur performance and thermal stability of two catalytic elements: Pt-Pd/γ-Al_2O_3, Pt-Pd/Ce-γ-Al_2O_3 and compared and analyzed our experimental results.

2 Experimental

2.1 Preparation of catalysts

A parallel flow dripping precipitation method was used to prepare a catalyst of Pt-Pd complex oxides. Its specific preparation process follows. A mixed solution of $H_2PtCl_6 \cdot 6H_2O$ and $PdCl_2$ was prepared in a mole ratio of 1:2 and placed in a beaker[6]. A NaOH solution was also prepared and placed in another beaker. Both solutions were then simultaneously added dropwise via a peristaltic pump to a third beaker which was pre-filled with a sodium bicarbonate buffer solution. This final solution was stirred violently before being put aside for 24 h for aging. The sample was then washed with de-ionized water and filtered before the solid obtained was dried and calcined for 4 h, when the sample of the Pt-Pd nanometer catalyst was obtained. The pH of the solution

Received 12 February 2010; accepted 21 May 2010
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doi: 10.1016/S1674-5264(09)60306-9

was controlled during the entire preparation process. The solution was mixed with $H_2PtCl_6 \cdot 6H_2O$ and $PdCl_2$ dropped on a large bicarbonate buffer solution, sufficient to stabilize the pH at 9, generating a uniform Pd-Pt nanometer complex oxide by depositing Pt, Pd metallic ions simultaneously.

2.2 Vector preparation

The following raw materials were used: $Al(NO_3)_3$ AR (Xuzhou MOL Medical Reagent Factory), HCL AR (Xuzhou MOL Medical Reagent Factory), $Ce(NO_3)_3 \cdot 6H_2O$ AR (Xuzhou Industry and Trade Company), $C_{18}H_{29}NaO_3S$ AR (Xuzhou Industry and Trade Company).

A Sol-Gel method was used in the experiment since it yields products of high purity, homogeneity, both well-controlled properties. $Al(NO)_3$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in absolute ethanol, a certain amount of SDBS (sodium dodecyl benzene sulfonate) was added before the ammonia solution was added dropwise in this mixture. The final solution obtained was stirred for 3 h and aged for 24 h before being filtered. After being washed and supercritical dried with ethanol as medium (260 °C, 8 MPa), the sample of aerogel CeO_2-γ-Al_2O_3 obtained was calcined for 3 h at temperatures of 500 and 1000 °C, our method of preparing multi-component powder of the nanometer CeO_2-γ-Al_2O_3[7].

A pure nanometer Al_2O_3 powder was prepared in the same way.

2.3 Preparation of catalytic elements

Both vectors, CeO_2-γ-Al_2O_3 and pure γ-Al_2O_3, were mixed with adhesive and coated with spiral platinum wire, before being burned in a muffle furnace based on a predetermined curve. The elements needed to be immersed in the Pt-Pd multi-component catalyst before being dried and aged with a 10% high CH_4 concentration for 15 min. This process was repeated three times before the elements were spot welded, yielding Pt-Pd/CeO_2-γ-Al_2O_3 catalytic elements.

Other catalytic elements were prepared with the pure Al_2O_3 nanometer in the same way, i.e., dried and aged under similar conditions. After being welded, catalytic elements made with pure γ-Al_2O_3 were prepared.

Some white elements were prepared similarly without being immersed in Pt-Pd.

The prepared white and black elements were matched by a dynamic matching method. The best matched elements were encapsulated with epoxy resins and connected as an electrical bridge[8]. Four units needed to be prepared for this experiment ($Bridge_{Ce1}$, $Bridge_{Ce2}$ stand for two bridges containing Pt-Pd/Ce-γ-Al_2O_3 catalytic elements; $Bridge_{Al1}$, $Bridge_{Al2}$ stand for two bridges containing Pt-Pd/γ-Al_2O_3 catalytic elements).

The electrical bridge made up with prepared elements is shown in Fig. 1. R_1 was prepared without the Pt-Pd catalyst and R_2 as black elements, while r_0 is an adjustable resistor used for adjusting the zero point of the electrical bridge.

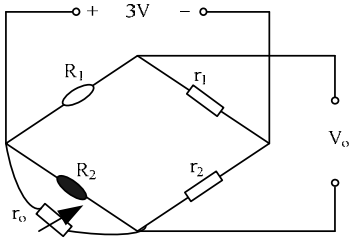

Fig. 1 Electrical bridge

2.4 Sensitivity and stability experiment[9]

The experimental system for sensitivity and thermal stability of methane sensors is shown in Fig. 2. Different gas samples were entered from the pipe, a 3.0 V constant voltage was loaded on the electrical bridge from a constant voltage source, in order to limit the error caused by fluctuation and attenuation. The output of the electrical bridge was read by an AOIP high precision digital multi-meter.

The two unit prepared electrical bridges ($Bridge_{Ce1}$, $Bridge_{Al1}$) were placed in a chamber before being preheated for 10 min; the working point and zero point were adjusted in clean air. Standard 1.5% CH_4 was piped in for 3 min, at a calibrated flow rate, after which the output was measured and recorded. The zero drift was checked before another standard 2.5% CH_4 was piped in for 3 min, also at a calibrated flow and the output measured and recorded. The zero point of the electrical bridges was not adjusted during the experiment.

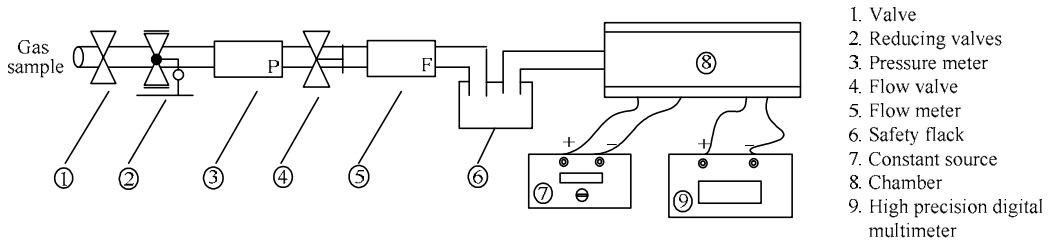

Fig. 2 Experimental system for sensitivity and stability