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Catalytic combustion of methane over supported bimetallic Pd catalysts: Effects of Ru or Rh addition

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Abstract

A series of Pd/γ-Al_2O_3 catalysts with various amounts of Ru or Rh with, and/or without, BaO were prepared by successive incipient wetness impregnation. The catalysts were investigated for the catalytic methane combustion before, and after, H_2S poisoning in an oxygen-rich atmosphere. The addition of ruthenium enhanced the catalytic activity for methane oxidation even after H_2S poisoning while maintaining the initial catalytic activity of the fresh catalyst. These results are explained in terms of dispersion of palladium by ruthenium and poisoning resistance of ruthenium. The addition of rhodium did not improve the overall activity in methane oxidation.

Keywords: Catalytic combustion; Methane; Palladium; Ruthenium; Rhodium; Barium oxide; Poisoning; Bimetallic catalyst

1. Introduction

The catalytic oxidation of hydrocarbons is an important technology for reducing pollutant emissions from combustion processes. Catalysts used in the combustion device promote the complete oxidation of the hydrocarbons and improve the energy efficiency of the process. Conventional noble-metal catalysts may become deactivated and/or poisoned in the presence of sulfur, halogens, phosphorus, arsenic and some metals. The thermal stability of catalysts is also a matter of concern, as catalysts can sinter at high temperatures. Among the noble-metal catalysts, supported palladium has been recognized as the most active catalyst for methane combustion [1] with thermal stability [2], but deactivating with sulfur-poisoned fuels, such as natural gas (LNG) [3].

Recently, Arcoya et al. [4] have reported that the sulfur resistance of the Group 8–10 metal catalysts increased in the following order, $Pt<Pd<Ni\ll Rh\leq Ru$, and that the catalyst life decreased in the order $Rh\geq Ru\gg Pd\geq Ni>Pt$ in ethylbenzene hydrogenation. However, it is rarely found in the literature that ruthenium or bimetallic ruthenium catalysts were tested for the application of catalytic methane combustion.

In the present paper, we report on preliminary results of the catalytic activities of the bimetallic catalysts (Ru or Rh/Pd) and the resistance to hydrogen sulfide for methane combustion in the 200–700°C range and also on the catalytic activities of two series of γ-alumina-supported Ru/Pd bimetallic catalysts.

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2. Experimental

2.1. Catalyst preparation

The bimetallic catalysts were prepared by successive impregnation of either γ-alumina (Sumitomo Chemical, Japan, Model AKS-GT-20, BET surface area ~160 m^2/g) or promoted γ-alumina which contained 5 mol% of BaO. An appropriate amount of $RuCl_3$ or Rh–CA (Engelhard) was impregnated first into the supports and excess water was removed by rotary-evaporation followed by drying at 110°C for more than 3 h. The loaded supports were finally calcined in air at 550°C for 2.5 h. The solids thus obtained were subsequently impregnated with aqueous Pd–CA solution and treated in the same way as described above. The calcined bimetallic catalysts were reduced at 450°C for at least 2.5 h in a flow of 8 vol% H_2 in nitrogen.

Two series of Ru–Pd/γ-Al_2O_3 were similarly prepared with a fixed load of palladium (1 or 3 wt%) and a varying load of ruthenium (1–5 wt%). All the reduced catalysts were stored in a sample bottle before activity tests.

2.2. Measurements

A fixed-bed laboratory-scale microreactor system was used in this study. Fig. 1 shows a schematic diagram of the reactor system. The reactor consists of a 15-mm ID and 40-cm long quartz tube. The reactor was heated in an IR-furnace in which four IR lamps (2 kW each) were mounted. The temperature was controlled to ±1°C by a temperature controller.

The catalyst bed (2 ml, 20–40 mesh), supported on a stainless-steel gauze on top of quartz wool, was placed in the center of the heated zone of the furnace. The temperature of the catalyst bed was monitored with a thermocouple protected by a quartz tube inserted in the center of the catalyst bed with its tip located a few millimeters (ca. 5 mm) below the top of the catalyst bed.

The gas flow rates were controlled by mass flow controllers (MFCs). The flow rate of the total feed of 1.4 l/min yielded a space velocity of 42 000 h^{-1}. The feed stream contained a mixture of 1 vol% CH_4 (99.9% purity)/air and was passed downward through catalyst pellets. A portion of the mixed feed stream was continuously vented through a 10-port valve. This

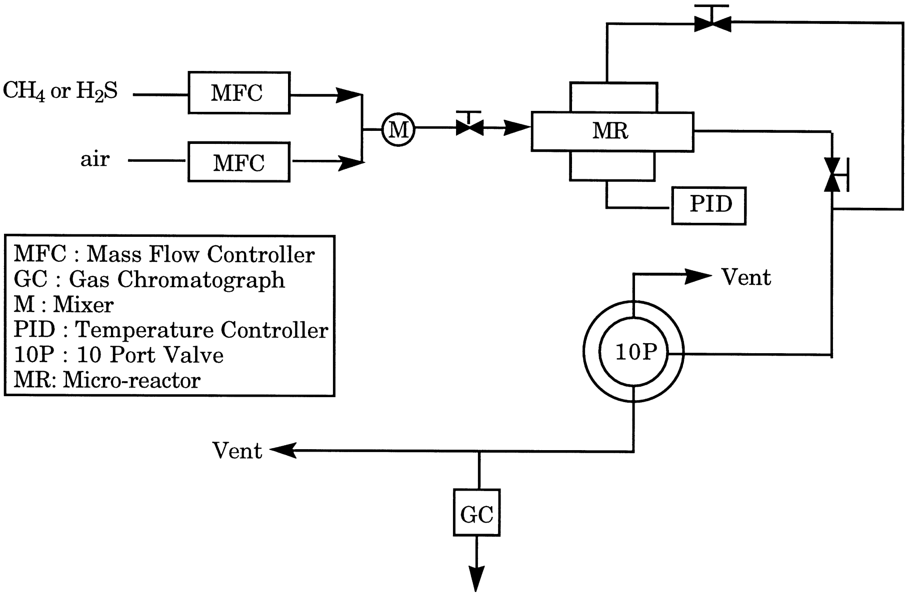

Fig. 1. Schematic diagram of the reactor system.

valve arrangement allowed for the analysis of either the feed or the effluent gas without disrupting the gas flow to the reactor. The feed (1 vol% CH_4) or the effluent gases were analyzed by an HP 5890 gas chromatograph (molecular sieve 13X(45/60) and Hayesep N(80/100) column) [carrier gas He (30 ml/min, initial temperature 30°C (1.5 min), rate 10°C/min, and final temperature 130°C (1 min)]. Products were detected either by a TCD for O_2 and N_2 or a FID for CO, CO_2 and methane. A methanizer (NiO/Al_2O_3) at 375°C was used in order to allow the detection of carbon monoxide and carbon dioxide by FID. The experimental parameters, such as reactor temperature, inlet gas concentration, flow rate and GC on/off, were all controlled by a computer program and monitored by a personal computer.

The activity of the fresh catalyst was measured as a function of the temperature between 200° and 700°C at temperature steps of either 25° or 50°C in a typical heating-and-cooling cycle run. Each temperature was maintained for 30 min (at least 15 min) and then the effluent gases were analyzed by GC.

With the H_2S poisoning experiments, the fresh catalysts were exposed to a flow containing 100 ppm of H_2S (5.21% H_2S/N_2 diluted with air) for 5 h at 500°C. The poisoned samples were then cooled to room temperature under flowing air. The activity was then measured with methods similar to those for the fresh sample with the sulfur-free mixture.

The metal contents of some of the catalysts were analyzed by ICP. The agreement between the nominal and analyzed loading was good. The surface areas were calculated by the BET equation, employing nitrogen adsorption at liquid nitrogen temperature (Quantasorb, Quanta-Chrome). All samples were degassed at 300°C for 3 h before measuring the surface area. The BET surface areas of the Ru or Rh/Pd/BaO(x)–γ-Al_2O_3 and x wt% Ru/1 wt% Pd/γ-Al_2O_3 catalyst were about 150 and 140 m^2/g, respectively, and that of the 1.5 wt% Ru/3 wt% Pd/γ-Al_2O_3 catalyst – 150 m^2/g.

3. Results

3.1. Effects of Ru or Rh addition and aging with hydrogen sulfide

Activity experiments with fresh and poisoned Ru (or Rh)/Pd/BaO(x)–Al_2O_3 catalysts were carried out

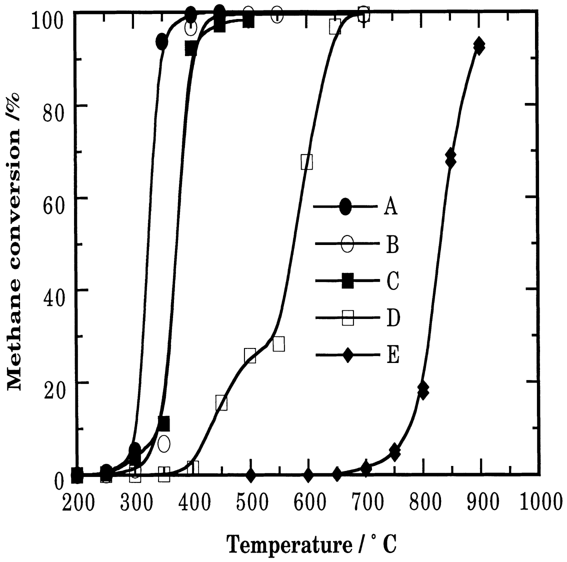

Fig. 2. Catalytic activity of fresh and poisoned Ru/Pd/BaO(x)–γ-Al_2O_3 catalysts in the catalytic methane combustion. (A) Fresh (x=0 mol%, Ru/Pd=1.5/3 wt%); (B) same as (A) but poisoned with H_2S; (C) fresh (x=4 mol%, Ru/Pd=1.7/2 wt%); (D) same as (C) but poisoned with H_2S; and (E) pure γ-alumina.

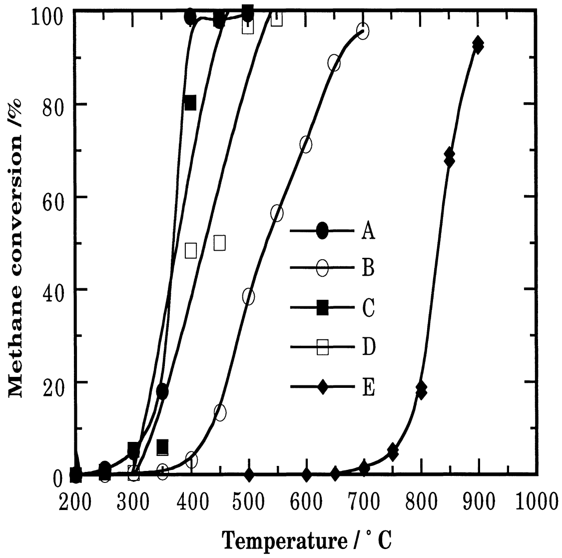

Fig. 3. Catalytic activity of fresh and poisoned Rh/Pd/BaO(x)–γ-Al_2O_3 catalysts in the catalytic methane combustion. (A) Fresh (x=0 mol%, Rh/Pd=1.5/1 wt%); (B) same as (A) but poisoned with H_2S; (C) fresh (x=5 mol%, Rh/Pd=0.26/0.7 wt%); (D) same as (C) but poisoned with H_2S; and (E) pure γ-alumina.

to investigate the effects of ruthenium or rhodium addition to the palladium-based catalyst with, and without, BaO in the alumina support. The results of the experiments are shown in Figs. 2 and 3. These figures also include the activity of pure γ-alumina (curve E) for comparison purposes.

According to Fig. 2, there is an abrupt rise in activity at a fixed reaction temperature. For the fresh sample of the Ru/Pd/γ-Al_2O_3 catalyst (curve A), the conversion at 320°C was 50% and an almost complete conversion was observed at 356°C. The light-off temperature was ca. 300°C for the fresh catalyst. For the H_2S-poisoned Ru/Pd/γ-Al_2O_3 catalyst (curve B), the light-off curve showed a behavior similar to that of the fresh catalyst, except that the overall methane conversion level was shifted by ca. 50°C. Addition of BaO to the Ru/Pd/γ-Al_2O_3 catalyst (curve C), however, lowered the catalytic activity for the combustion of methane. The fresh sample of the Ru/Pd/BaO–γ-Al_2O_3 catalyst showed a conversion plot shifted by ca. 40°C as compared to that of the fresh Ru/Pd/γ-Al_2O_3 catalyst, but similar to that of the H_2S-poisoned Ru/Pd/γ-Al_2O_3 catalyst represented in Fig. 2 (curves B and C). A drastic decrease in activity, leading to a shift of 200°C, was found for the poisoned Ru/Pd/BaO–γ-Al_2O_3 catalyst (curve D). A slow increase in conversion with temperatures up to 550°C and then a rather smooth increase is observed. Complete conversion of methane by the poisoned catalyst occurred at ca. 640°C, which is still far below the temperature at which pure alumina exhibited the complete conversion. The complete conversion of methane with other catalysts occurred below 450°C. Table 1 summarizes the methane combustion activity of bimetallic Ru/Pd/BaO(*x*)–γ-Al_2O_3 catalysts. In Table 1, the combustion activity is expressed as the temperatures, T_{10}, T_{50} and T_{90}, at which the methane conversion reaches 10, 50 and 90%, respectively.

Fig. 3 shows the catalytic activity of methane combustion over the fresh and poisoned Rh/Pd/BaO(*x*)–γ-Al_2O_3 catalysts. The results of the catalytic activities are also summarized in Table 1. The overall catalytic activity of rhodium bimetallic catalysts turned out to be lower than those of Ru/Pd/BaO(*x*)–γ-Al_2O_3 catalysts. The fresh sample of Rh/Pd/–γ-Al_2O_3 catalyst showed a light-off temperature (∼320°C) comparable with that of the Ru/Pd analog. The activity of the Rh/Pd catalyst rose, however, less steeply with the temperature as compared to that of the Ru/Pd catalyst (curves A in Figs. 2 and 3). The poisoned sample of the Rh/Pd/–γ-Al_2O_3 catalyst (curve B) showed a poor activity like the Ru/Pd/BaO–γ-Al_2O_3 catalysts. It is noteworthy that addition of BaO to the Rh/Pd/γ-Al_2O_3 catalyst changed the activity for methane combustion differently from that of the Ru/Pd/γ-Al_2O_3 catalyst. It was found that the activities of the fresh and poisoned BaO-promoted catalysts improved relative to that of the unpromoted analog (curves C and D).

3.2. *Catalytic activities of the bimetallic Ru/Pd catalysts of low and high Pd loading*

Two series of Ru(*x*)/(1 or 3 wt% Pd)/γ-Al_2O_3 catalysts in which the palladium loading was fixed at 1 wt% (low loading) or 3 wt% (high loading) and the ruthenium loading was varied from 0 to 5 wt% were tested for the catalytic activity of methane combustion between 200° and 700°C with heating-up and heating-down cycles run during ca. 24 h.

Fig. 4 shows some typical results of the bimetallic catalysts [Ru(*x*)/1 wt% Pd/γ-Al_2O_3] of a low Pd loading. Table 2 summarizes the catalytic methane combustion activity of bimetallic Ru/1 wt% Pd/γ-Al_2O_3

Table 1
The catalytic methane combustion activity of the bimetallic Ru (or Rh)/Pd/BaO(*x*)–γ-Al_2O_3 catalysts

Catalysts	T_{10}(°C)		T_{50}(°C)		T_{90}(°C)	
	fresh	poisoned	fresh	poisoned	fresh	poisoned
Pure Al_2O_3	750		830		890	
Ru/Pd/Al_2O_3	300	340	320	370	356	404
Ru/Pd/BaO–Al_2O_3	335	425	370	570	400	636
Rh/Pd/Al_2O_3	323	430	370	526	392	652
Rh/Pd/BaO–Al_2O_3	348	348	378	424	418	492

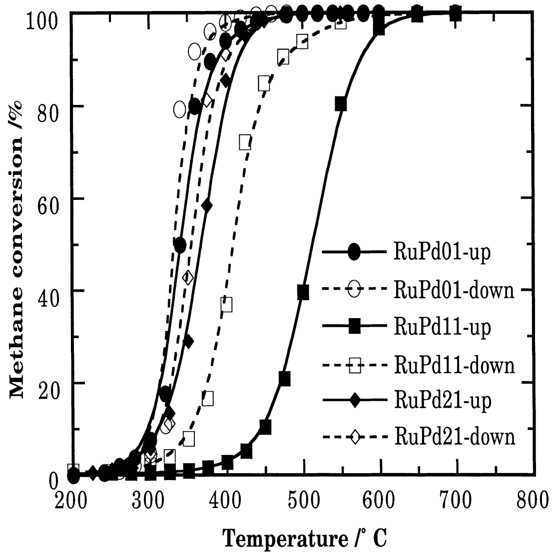

Fig. 4. Catalytic combustion of methane on *x* wt% Ru/1 wt% Pd/γ-Al_2O_3 catalysts (*x*=0, 1 or 2).

catalysts. All the catalysts showed the same trend. The reference catalyst, RuPd01, displayed a low light-off temperature of ca. 310°C. There is a small increase in the methane conversion at high levels from an initial heating run to a cooling run. All other catalysts except RuPd0.51 and RuPd51 showed hystereses between the initial heating and cooling runs. It was observed that the cooling run exhibited a higher activity. The largest hysteresis was found for the RuPd11 catalyst with a difference of 90–100°C at both ends of the light-off curve shown in Fig. 4. The RuPd31 catalyst also showed a large hysteresis. It is remarkable that the best catalytic activity of this series of catalysts (RuPd21) was still lower than that of the reference catalyst (RuPd01).

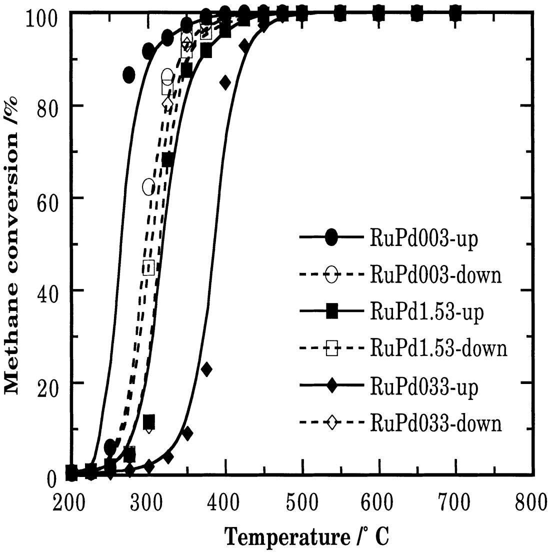

Fig. 5. Catalytic combustion of methane on *x* wt% Ru/3 wt% Pd/γ-Al_2O_3 (*x*=0, 1.5 or 3).

Fig. 5 shows some typical results of the bimetallic catalysts [Ru(*x*)/3 wt% Pd/γ-Al_2O_3] of the high Pd loading. Table 3 summarizes the catalytic activity in methane combustion of the bimetallic catalysts at the high Pd loading. All catalysts showed the same trend, except the reference catalyst (RuPd003). The reference catalyst, RuPd003, exhibited a low light-off temperature of 250°C and almost complete conversion of methane at 300°C in a heating run, but the conversion plot in a cooling run shifted to higher temperatures by 15° to 40°C. The hysteresis was more propound as the methane conversion increased. Other catalysts also displayed hystereses between a heating and cooling run. However, the catalytic activities in a cooling run were better (by 20°C) than those in a

Table 2
The catalytic methane combustion activity of *x* wt% Ru/1 wt% Pd/Al_2O_3 catalysts

Sample	Catalysts (Ru/Pd, wt%/wt%)	T_{10}(°C)		T_{50}(°C)		T_{90}(°C)	
		heating up	heating down	heating up	heating down	heating up	heating down
RuPd01	Pd/Al_2O_3 (0/1)	304	316	340	330	380	355
RuPd0.51	RuPd/Al_2O_3 (0.5/1)	370	370	409	397	445	445
RuPd11	RuPd/Al_2O_3 (1/1)	440	350	511	408	573	474
RuPd21	RuPd/Al_2O_3 (2/1)	320	320	366	354	415	400
RuPd31	RuPd/Al_2O_3 (3/1)	390	326	438	366	488	426
RuPd41	RuPd/Al_2O_3 (4/1)	366	344	406	392	438	438
RuPd51	RuPd/Al_2O_3 (5/1)	350	350	388	388	425	425

Table 3
The catalytic methane combustion activity of *x* wt% Ru/3 wt% Pd/Al_2O_3 catalysts

Sample	Catalysts	T_{10}(°C)		T_{50}(°C)		T_{90}(°C)	
	(Ru/Pd, wt%/wt%)	heating up	heating down	heating up	heating down	heating up	heating down
RuPd01	Pd/Al_2O_3 (0/1)	304	316	340	330	380	355
RuPd003	Pd/Al_2O_3 (0/3)	250	270	265	295	300	338
RuPd0.53	RuPd/Al_2O_3 (0.5/3)	324	290	370	313	412	345
RuPd013	RuPd/Al_2O_3 (1/3)	310	285	360	312	415	345–350
RuPd1.53	RuPd/Al_2O_3 (1.5/3)	294	277	316	302	366	344
RuPd023	RuPd/Al_2O_3 (2/3)	320	270	364	290	410	320
RuPd033	RuPd/Al_2O_3 (3/3)	340	290	384	313	420	340

heating run. The largest hysteresis was found for the RuPd033 catalyst, similar to that of bimetallic catalyst of a low Pd loading (Table 3). It was also established that all the bimetallic catalysts of a high Pd loading showed very good catalytic activities, which were all comparable to that of the reference catalyst, and an even better catalytic activity was obtained with the catalyst RuPd023 (see Fig. 5 and Table 3). The light-off temperature and the temperature of almost complete conversion of the catalyst RuPd023 in the cooling run were 270° and 320°C, respectively.

4. Discussion

The preliminary results indicate that addition of ruthenium metal to palladium is beneficial to maintain the catalytic activity of palladium and increases the poison resistance of palladium catalysts. There is no clear evidence that Rh/Pd bimetallic catalysts exhibit an improved catalytic activity and poison resistance as compared to palladium catalysts. Oh et al. [5] have reported the effects of addition of rhodium on the methane oxidation behavior of alumina-supported palladium catalysts. The addition of small amounts of rhodium did not significantly change the temperature required for the onset of the methane oxidation, in agreement with our results even though the rhodium load is much higher here (0.15–0.3 wt%).

The effects of BaO addition on the methane conversion behavior of bimetallic catalysts showed contrasting results: the addition of BaO decreases the catalytic activity of fresh and poisoned Ru/Pd bimetallic catalysts, whereas it increases that of Rh/Pd catalysts. It is not clear, at present, what causes such different behavior. Our calcination temperature of the catalysts and our reaction conditions may not have been sufficient to effect a BaO–support interaction. This might simply imply that superficial BaO in Ru (or Rh)/Pd bimetallic catalyst partially covers active sites and blocks the accessibility of reactants differently with each bimetallic catalyst.

From the rather extensive study of Ru/Pd bimetallic catalysts, the most promising effect is the absence of the significant drop of methane conversion due to addition of Ru. The bimetallic catalyst of a high Pd loading could, thus, maintain its catalytic activity at a similar level as the reference Pd catalyst. Poirier et al. [6] have reported the catalytic activity of a 1% Ru/γ-Al_2O_3 catalyst being about 40% of that of 1% Pd/γ-Al_2O_3 catalyst in methane combustion. Viniegra et al. [7] have reported that addition of Pd to an Ru/SiO_2 catalyst increased the catalytic activity in the hydrogenation of benzene due to dilution of ruthenium ensembles by palladium. Direct evidence for mutual dispersion or dilution of Ru and Pd metal was recently obtained from elegant work performed by Pinna et al. [8] using TPR and WAXS (wide angle X-ray scattering) experiments. These authors observed that addition of Ru, even in very small percentages, increased the Pd dispersion in Pd/C catalysts, while there was no obvious electronic interaction between Pd and Ru. All these results and the sulfur resistance mentioned in Section 1 are in good agreement with our results, suggesting that addition of ruthenium increases not only the dispersion of alumina-supported palladium, but increases the stability of the palladium ensembles in a such way as to impede the exposure of bare palladium atoms to poisonous gases, such as H_2S.

5. Conclusions

The role of the addition of Ru or Rh with, and without, BaO regarding the catalytic methane combustion has been investigated for Pd/γ-Al_2O_3 base catalysts. Addition of Rh with, and without, BaO did not noticeably improve the catalytic activity of Pd/γ-Al_2O_3 catalysts in methane combustion. On the other hand, addition of Ru to Pd/γ-Al_2O_3 catalysts enhances the H_2S poison resistance without any significant negative effect on the catalytic activity. It is suggested that Ru metal maintains the integrity of the catalytic activity of the Pd catalyst and block the accessibility of poisonous H_2S to active Pd sites. Thus, an Ru/Pd bimetallic catalyst can be a good poison-resistant catalyst for the catalytic combustion of natural gas at temperatures below 700°C. It could be replace the expensive Rh catalyst in industrial application.

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