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Letter

Au–Pt/Co$_3$O$_4$ catalyst for methane combustion

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Abstract

The catalytic activity of Au/Co$_3$O$_4$ (Au loading was 2–5 wt.%) towards methane combustion could be enhanced when small amount of Pt, e.g. 0.2 wt.% was added, and the temperature for 100% conversion of methane could be decreased by 50°C. Palladium, which was the most active single metal catalyst for methane combustion, on the other hand, exhibited lower catalytic activity than Au–Pt/Co$_3$O$_4$ when combined with Au over the Co$_3$O$_4$ support. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Catalytic combustion; Au–Pt/Co$_3$O$_4$

1. Introduction

Natural gas, which consists primarily of methane, had been receiving much attention as an alternative fuel for motor vehicles and power plants [1,2]. Methane combustion at sufficiently low temperatures can be achieved only by the application of highly active noble metal catalysts. Palladium has been well known as the most active material for the combustion of methane [3–5], and much research on methane combustion over Pd catalysts has been made in the past decade [6–9]. From the point of view of fundamental research and practical application, it is still highly desirable to develop a catalyst with higher activity to initiate methane combustion at a temperature as low as possible.

Gold as a catalyst has attracted little attention because of its inert character and low melting point (1063°C). However, since Haruta et al. reported in 1987 that some gold catalysts prepared by coprecipitation were extraordinarily active for the low-temperature oxidation of CO [10], gold catalysts have received growing attention and many reactions catalyzed over Au catalyst with high activity were reported [11–13]. Although, it was already reported that coprecipitated Au on several transition metal oxides was remarkably active in the total oxidation of methane [14], the potential of Au catalyst for the combustion of methane has not yet been paid much attention.

In this work, the Au/Co$_3$O$_4$ catalysts modified with Pt and Pd were prepared and investigated for methane combustion, aiming to find better catalysts containing Au for methane complete combustion at lower temperature.

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2. Experimental

2.1. Catalyst preparation

All chemicals used in the experiments were analytical grade. The Au–Pt/Co_3O_4 and Au–Pd/Co_3O_4 catalysts with different Au, Pt and Pd loading were prepared by coprecipitation technique. Under stirring, an aqueous mixture of $HAuCl_4 + H_2PtCl_6$ (or $HAuCl_4 + H_2PdCl_4$) with cobalt nitrate was dropwise added into Na_2CO_3 solution and the pH of the finally resulted solution was controlled to ca. 8. The resulted precipitate was filtrated, and washed with distilled water several times to remove chloride ions. The precursor was dried at 120°C overnight and finally calcined in air at 400°C for 5 h. Au/Co_3O_4, Pd/Co_3O_4, Pt/Co_3O_4 and Co_3O_4 were also prepared in this manner. The catalysts mentioned above were tested for methane oxidation without any further reduction treatment. For comparison, Pd/Al_2O_3 catalysts with ca. 1.6–3.7 wt.% palladium loadings were also prepared by incipient wetness impregnation with aqueous solution of $Pd(NO_3)_2$ so as to avoid any possible contamination of chloride ions which may be detrimental to the catalytic activity towards methane combustion. After impregnation, the dried precursor was calcined in air at 500°C for 5 h and reduced in H_2 at 400°C for 3 h. The concentrations of Au, Pt and Pd in catalysts were analyzed with 3520 ICP AES instrument (ARL Co., USA). X-ray diffraction of these catalysts particles was performed on a Siements D/max-RB powder X-ray diffractometer and BET surface area were obtained using a Micromeritics ASAP 2010 instrument.

2.2. Catalytic activity measurements

Catalytic activity measurements were conducted using a fixed bed microreactor charged with 0.10 g of catalyst (60–80 mesh). Before measurements, the catalyst was treated with flowing air at 400°C for 1 h, and then, a gas mixture containing 1 vol.% CH_4, 5 vol.% O_2, and N_2 balanced was fed to the reactor at 150°C with hourly space velocity of 10,000 per hour. The reaction temperature was continuously increased with the rate of 4°C/min until no methane from the outlet of reactor could be detected, and if necessary, the methane was further monitored with temperature

decreasing. Methane concentration from inlet and outlet of reactor was analyzed using on-line HP 6890 gas chromatography equipped with a micro-thermal conductivity detector and HP-PLOT column (Molecular sieve 5A).

3. Results and discussion

The test of methane combustion for each catalyst had been conducted at lest two times, and repeated results could be obtained. The activities of Co_3O_4, supported Au, Pt, Pd, Au–Pt and Au–Pd catalysts for methane combustion, which are presented as the temperatures at which methane conversion is 2 (defined as light-off temperature), 50, 90 and 100%, respectively, were listed in Table 1. It can be seen that Co_3O_4 itself exhibited moderately high activity for methane combustion, which was consistent with the result reported previously [15]. The catalytic activities were increased with varied ranges when Au, Pt and Pd was, respectively, incorporated into Co_3O_4, and slightly increased when the loading of the noble metals was increased from ca. 0.2 to 2 wt.% (entries 2–7). The activities of these catalysts were in the order Pd/Co_3O_4 > Pt/Co_3O_4 > Au/Co_3O_4. It was also confirmed that Pd is more active for methane oxidation than Pt.

Surprisingly, the activity of Au/Co_3O_4 for methane combustion was enhanced when Pt was incorporated even if the Au and Pt loading was relatively lower (entry 8). The temperatures of light-off and 100% methane conversion were further decreased with increasing Au and Pt loading (entries 9 and 10) and seemed to reach a minimum value (entry 10), i.e. methane could be oxidized at ca. 218°C and could be completely oxidized at ca. 360°C. It can be concluded that there exists synergism between Pt and Au, which could enhance the activity of methane combustion. Moreover, the activity for methane oxidation would be slightly reduced when the Au loading reached ca. 5 wt.% (entry 11), indicating that there may exist an optimized ratio for Au and Pt loading.

Since Pd/Co_3O_4 is the most active catalyst for methane combustion among the Co_3O_4 supported Au, Pt, and Pd, Au–Pd/Co_3O_4 catalyst was also tested for methane oxidation (entry 12). The activity of Au–Pd/Co_3O_4 at higher temperatures was a little enhanced in comparison with Au/Co_3O_4 (entry 3), but

Table 1
Catalytic performances for methane combustion over supported noble metal catalysts

Entry	Catalyst	Au content (%)	Pt or Pd content (%)	BET (m^2/g)	Catalytic activity (°C)			
					$T_{light-off}$	T_{50}	T_{90}	T_{100}
1	Co_3O_4	–	–	57.1	250	325	376	420
2	Au/Co_3O_4	0.18	–	55.3	241	317	370	420
3	Au/Co_3O_4	1.91	–	52.2	241	314	369	418
4	Pt/Co_3O_4	–	0.21	64.5	238	312	358	400
5	Pt/Co_3O_4	–	1.96	72.6	235	308	348	385
6	Pd/Co_3O_4	–	0.19	62.3	228	307	350	392
7	Pd/Co_3O_4	–	1.92	66.2	224	304	338	376
8	$Au–Pt/Co_3O_4$	0.38	0.23	59.2	228	305	340	379
9	$Au–Pt/Co_3O_4$	1.90	0.19	59.8	232	303	338	368
10	$Au–Pt/Co_3O_4$	1.92	1.63	61.0	218	295	332	360
11	$Au–Pt/Co_3O_4$	4.76	1.67	64.1	222	296	336	364
12	$Au–Pd/Co_3O_4$	1.90	1.48	48.5	241	317	363	388
13	Pd/Al_2O_3	–	1.58	139.8	264	338	367	387
14	Pd/Al_2O_3	–	3.70	132.5	251	313	339	358

slightly reduced in comparison with Pd/Co_3O_4 (entry 7). Gold may inhibit the Pd activity for methane oxidation when they are combined together.

Though not shown here, the typical results of methane conversion versus temperature programmed run-up and then run-down over $Au–Pt/Co_3O_4$ showed that, the catalytic activity during the followed temperature run-down was slightly higher than that during temperature run-up, which indicated that no deactivation could be observed, which was different with the result of Au/Al_2O_3 reported previously [16].

At the same reaction conditions, the activities of Pd/Al_2O_3 catalysts prepared by incipient wetness impregnation with aqueous solution of $Pd(NO_3)_2$ for the total oxidation of methane were also examined. It can be seen that the activity of Pd/Al_2O_3 with 1.58 wt.% loading (entry 13) was lower than that of the $Au–Pt/Co_3O_4$ catalyst (entry 12), and the activity of Pd/Al_2O_3 with 3.70 wt.% loading could be comparable with that of $Au–Pt/Co_3O_4$ catalyst in methane combustion.

Measurements of BET surface area of the catalysts showed that moderately high surface area of pure Co_3O_4 was obtained by coprecipitation. The surface area could be further enlarged when Au and Pt were incorporated into the Co_3O_4, and increased continuously with increasing the loading of Au and Pt.

Characterization of the pure Co_3O_4 and $Au–Pt/Co_3$O$_4$ catalysts with relatively high Au loading (entry

11) by powder X-ray diffraction showed that neither Au nor Pt phases could be observed, although, the Au loading in the catalyst (entry 11) was 4.76 wt.%, and only Co_3O_4 was determined, indicating that both of Au and Pt was amorphous or highly dispersed on or in the Co_3O_4 support (Fig. 1). The influence of hourly space velocity on the catalytic performance of $Au–Pt/Co_3O_4$ catalyst (entry 11) was also carried out.
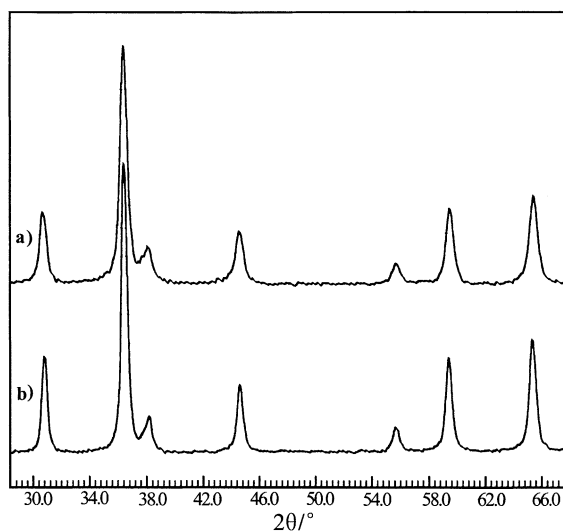

Fig. 1. XRD-pattern of pure Co_3O_4 and $Au–Pt/Co_3O_4$: (a) $Au–Pt/Co_3O_4$ (entry 11); (b) Co_3O_4.

The results showed that the $T_{\text{light-off}}$, T_{50} and T_{100} were, respectively, increased from 222, 296 and 364 to 250, 337 and 415°C when the hourly space velocity was adjusted from 10,000 to 30,000 per hour, indicating that a good catalytic performance could still be achieved at relatively higher hourly space velocity.

At this stage, the detailed mechanism on the interaction between Au and Pt on the Co_3O_4 support, which resulted in the enhancement in the activity towards methane combustion, is not clear, however, to the best of our knowledge, this is the first reported study of Au–Pt/Co_3O_4 catalyst prepared by coprecipitation for the methane combustion at lower temperature. The further optimization of Au–Pt/Co_3O_4 catalyst preparation for the methane combustion is now under way.

References

[1] D.L. Trimm, Appl. Catal. 7 (1983) 249.

[2] K. Sekizawa, H. Widjaja, K. Eguchi, Proc. Int. Workshop Catal. Combust. 4 (1999) 79.

[3] S.H. Oh, P.J. Mitchell, R.M. Siewert, J. Catal. 132 (1991) 287.

[4] J.G. Firth, H.B. Holland, Faraday Soc. Trans. 65 (1969) 1121.

[5] C.F. Cullis, B.M. Willat, J. Catal. 83 (1983) 267.

[6] G. Pecchi, P. Reyes, R. Gomez, T. Lopez, J.L.G. Fierro, Appl. Catal. B: Environ. 17 (1998) L7.

[7] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 280.

[8] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 359.

[9] Y. Deng, T.G. Nevell, J. Mol. Catal. A: Chem. 142 (1999) 51.

[10] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. (1987) 405.

[11] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566.

[12] L. Prati, M. Rossi, J. Catal. 176 (1998) 552.

[13] Q. Xu, Y. Imamura, M. Fujiwara, Y. Souma, J. Org. Chem. 62 (1997) 1594.

[14] R.D. Waters, J.J. Weimer, J.E. Smith, Catal. Lett. 30 (1995) 181.

[15] Z. Li, G.B. Hoflund, React. Kinet. Catal. Lett. 30 (1999) 36.

[16] R.J.H. Grisel, P.J. Kooyman, B.J. Nieuwenhuys, J. Catal. 191 (2000) 430.