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Oxidation of Carbon Monoxide and Methane over CeO_2-supported Palladium Catalysts†

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Dispersed PdO which interacts with CeO_2 is the active site for CO oxidation, while the large PdO particles which do not interact strongly with CeO_2 are the active site for methane oxidation.

Complete oxidation of carbon monoxide and gaseous hydrocarbons to carbon dioxide and water by catalysis has been used to reduce toxic emissions from car exhausts. Precious metals (Pt, Pd) are well known complete oxidation catalysts with high activity and stability. In the past several years, much interest has arisen in the use of ceria, CeO_2, as a precious and transition metal oxide support. For example, Pt/CeO_2 has been used for oxidation of CO[1] and ethylene,[2] and in the water-gas shift reaction.[3] However, virtually no study on CeO_2 as a support for palladium catalysts of carbon monoxide and methane oxidation has been reported. The present work is concerned with the oxidation activity of PdO–CeO_2 for carbon monoxide and methane.

Experimental

Preparation of Catalysts.—The CeO_2 was prepared by thermal decomposition of cerium(III) nitrate, $Ce(NO_3)_3$, for 4 h at 650 °C in air. Its BET surface area is 55 m^2 g^{-1}. The supported PdO–CeO_2 catalysts were prepared by the conventional wet impregnation method using an aqueous solution of H_2PdCl_4, dried overnight in an oven at 120 °C and then heated in air at 650 °C for 4 h. The loading of Pd was 0.25, 0.75, 1.5, 2.0, and 5.0%, respectively. The catalyst is denoted as PdO–CeO_2 (X%). The amount of chlorine included in the catalyst was too small to be detected by spectrophotometry.[4]

Activity Measurement.—Catalytic activity measurements were carried out in a fixed bed reactor (0.6 cm i.d.) using 150 mg of catalyst mesh size 20–60. The total gas flow rate was 80 (ml min^{-1}). For CO oxidation, the gas consisted of 2.4% CO and 1.2% O_2 in N_2, for methane oxidation, 2.8% CH_4 and 8% O_2 in N_2. The catalysts were directly exposed to 80 ml min^{-1} of reaction gas as the reactor temperature stabilized at reaction temperature, without any pretreatment. The products were analysed by gas chromatography with Molecular Sieves 13X and Porapak Q columns both operating at 50 °C.

Results and Discussion

Fig. 1 shows the catalytic activity of the PdO–CeO_2 catalyst in the oxidation of CO and methane. The activity was compared on the basis of T_{20} (the temperature for 20% conversion). None of these catalysts was pretreated before reaction. This is particularly important in applications where pretreatment is not possible or when the catalysts must be stored in air before use. The T_{20} of pure PdO for CO oxidation is 250 °C. The activity of pure PdO and CeO_2 is much lower than that of PdO–CeO_2 catalysts. The activity of the latter increases with palladium loading from 0.25 to 2%, but larger amounts of Pd (from 2 to 5%) do not affect the activity. Since the activity of pure PdO and the CeO_2 support is very low, a synergistic interaction between the two is responsible for the high activity for carbon monoxide oxidation at low temperature. On the basis of the results, only a small amount of palladium (2%) is needed to form the active site for CO oxidation, and the excess of Pd forms bulk PdO particles contributing little to the activity. In other words, the dispersed PdO which interacts with CeO_2 is the active site for CO oxidation. From Fig. 1, it can be seen that the activity of the catalyst at low palladium loading (0.25 and 0.75%) for methane oxidation is lower than that

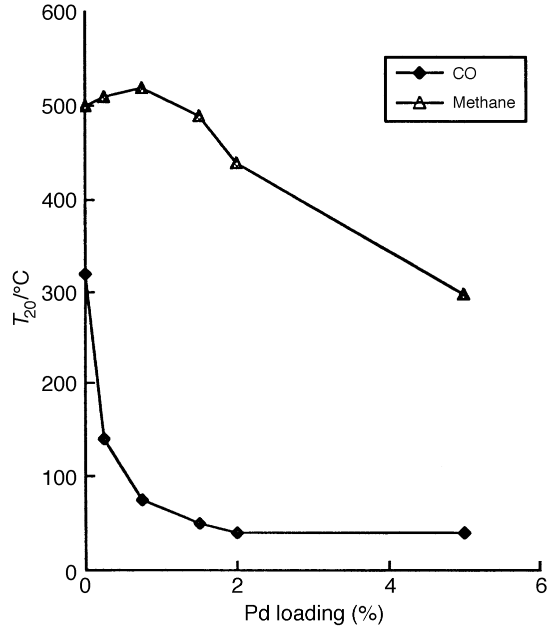

Fig. 1 Effect of palladium loading in PdO–CeO_2 catalyst on activity for CO and methane oxidation

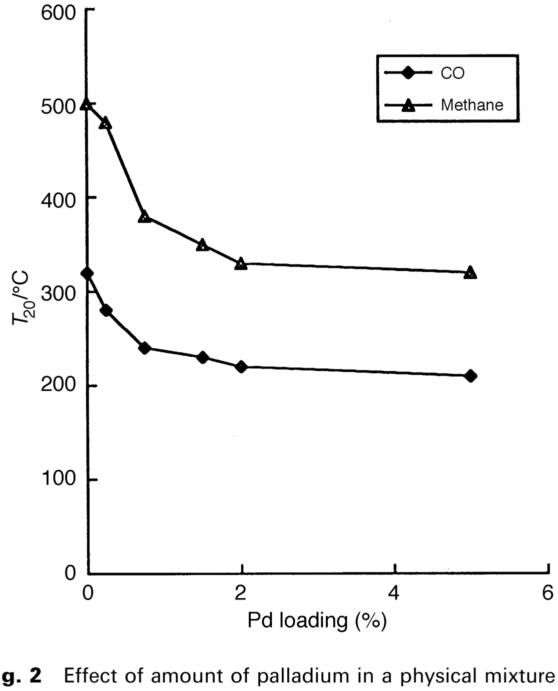

Fig. 2 Effect of amount of palladium in a physical mixture of PdO–CeO_2 on the activity for CO and methane oxidation

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of the CeO_2 support. As the loading increases from 1.5 to 5% the activity of the PdO–CeO_2 catalyst increases. We think that finely dispersed PdO is not active, and that the large particles of PdO are the active site for methane oxidation. This is consistent with the SiO_2, Al_2O_3 and SiO_2–Al_2O_3 supported palladium catalysts for methane oxidation reported by Muto *et al.*[5]

To clarify that the active site for CO and methane oxidation reaction is the finely dispersed PdO and the large particles of PdO respectively, the activity of a physical mixture of PdO–CeO_2 was investigated, as shown in Fig. 2. It is well known that the crystal particle size of PdO in a physical mixture is larger than that of a catalyst prepared by impregnation methods. Compared to Fig. 1, it is clear that the activity of the mixture for CO oxidation is much lower than that of the PdO–CeO_2 catalyst. Thus, we conclude that the finely dispersed PdO which interacts with CeO_2 mainly contributes to the catalytic activity for CO oxidation at low temperature, and the large particles of PdO contribute little to the activity. However, for methane oxidation, the catalytic activity of the mixture is much higher than that of the PdO–CeO_2 catalyst as the palladium loading increases from 0.25 to 2%, while the activity of the PdO–CeO_2 (5%) catalyst for methane oxidation is slightly higher than that of the PdO–CeO_2 (5%) mixture. The activity of the mixture obviously increases as the amount of Pd increases from 0.25 to 2%. This indicates that the large particles of PdO are the active site for methane oxidation.

In order to confirm the active site of the catalyst for CO and methane oxidation, we selected a low surface area CeO_2 support ($22\ m^2\ g^{-1}$). The T_{20} of this supported PdO catalyst (2%) for CO and methane oxidation is 55 and 420 °C, respectively. This indicates that the activity of the low surface area catalyst for CO oxidation is lower than that of the high surface area catalyst, while the activity of the former for methane oxidation is higher than that of the latter. We further conclude that the finely dispersed PdO is the active site for CO oxidation, the large particles of PdO that for methane oxidation.

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