Influence of acid–base property of support on the toluene combustion activity of palladium

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Received 12 August 1998; accepted 20 January 1999

Metal–support interaction in the catalytic combustion of toluene was studied, using metal oxides with different acid–base properties as supports. The combustion activity over Pd loaded on strong acidic or basic support was lower than over Pd on weak acidic or basic metal oxides. The study of Pd surface with X-ray photoelectron spectroscopy and reaction order measurement showed that the affinity for oxygen changed according to the acid–base property of support. It was considered that the combustion activity of Pd was controlled by the acid–base property of support through an electronic interaction.

Keywords: toluene combustion, acid–base property of metal oxide, metal–support interaction, X-ray photoelectron spectroscopy

1. Introduction

Recently, catalytic combustion of hydrocarbons is widely studied from the viewpoint of environmental protection. Sufficient activity is required for operation at low temperature with low emission of NO_x gas. Among the combinations of active metal and support oxide, Pd loaded on Al_2O_3 has been widely studied, in relation with the identification of active phase, reaction mechanism [1,2], and the structure sensitivity [3,4]. Though previous attention was primarily directed to the investigation on the active sites, the role of the support seems to be important. From the experiment with various metal oxides used as supports, Widjaja et al. reported that Pd loaded on SnO_2 had a high activity for the methane combustion [5]. In our study of Pd loaded on different kinds of zeolite, we reported that the combustion activity of Pd was strongly dependent on the Al concentration as well as the structure of the zeolites, implying that the acid sites generated on Al in the zeolite framework had a profound influence on the activity of Pd [6]. This fact means that the acid or base property of support is one of the important factors which determines some nature of supported Pd, such as dispersion or oxidation state of Pd. In the present study, in order to elucidate how the acid or base property of support affects the surface oxidation state and reactivity of Pd, Pd was loaded on five kinds of metal oxide with different acid or base character as supports. X-ray photoelectron spectroscopy and reaction order study were correlated with the combustion activity of toluene to find out the active phase in Pd and the role of the support oxide. The binding energy of Pd is sensitive to the change in Pd state [7,8] and the kinetic study gives information about the oxidation state of Pd surface under the reaction conditions [9]. Such a fundamental study on the interaction between metal and acid–base property of support may serve to understand one aspect of the metal–support interaction in the supported catalyst.

2. Experimental

Five kinds of metal oxide with 1–5 valence number, MgO (JRC-MgO-1, reference catalyst supplied from the Catalysis Society of Japan), Al_2O_3 (Wako Chemicals), SiO_2 (ox-50), Nb_2O_5 (Wako Chemicals), and WO_3 (Wako Chemicals), were employed as supports for Pd. Loading of Pd was conducted with a conventional impregnation method. The metal oxides were immersed in $PdCl_2$ aqueous solution and heated on a hot plate with stirring to remove the excess water. After drying, they were calcined for 4 h at 773 K under nitrogen flow. The loading of Pd was 0.5 wt% for every catalyst. Combustion of toluene was carried out by a fixed flow bed reactor. A 5 mg of sample diluted with 1 g of glass bead was used for the reaction. For the toluene combustion, a mixture of toluene/O_2/N_2 ($0.95:20:79$) was fed at 100 ml min^{-1} to the catalyst. The products were analyzed using a gas chromatograph equipped with a Silicone SE-30 column. The reaction order on the oxygen pressure was measured by changing the flow rate of oxygen and N_2 balance while holding the toluene pressure.

Surface area of the calcined Pd/metal oxide was measured by the BET method after pretreatment at 673 K. Pd dispersion was determined by CO adsorption conducted at 273 K under 13.3 kPa of CO. Before adsorption, the catalyst was reduced by 13.3 kPa of circulated hydrogen at 573 K. For the calculation of adsorbed CO on Pd, the physisorbed amount was subtracted from the total CO uptake.

X-ray photoelectron spectroscopy (XPS) was measured using a Shimadzu ESCA-1000 spectrometer. The catalyst was calcined under oxygen flow (20 ml min^{-1}) at 573 K for 1 h. Then the sample was pressed to wafer form and suspended on the sample mount. The charge compensation of the samples was controlled by referencing to the C 1s line at 284.8 eV.

3. Results and discussion

3.1. Combustion of toluene over supported Pd catalysts

The surface area and Pd dispersion listed in table 1 were relatively small and no correlation was observed between combustion activity and these parameters. Besides, the dispersion of Pd was low, thus the influence due to the Pd support interface was negligible.

Figure 1 shows the dependence of toluene conversion on the reaction temperature. The observed products were carbon dioxide and water, meaning complete combustion occurred on the catalysts. Pd on MgO and WO_3, which has strong basic or acidic character, were relatively inactive to the reaction, while metal oxides with weak acid–base property, such as Al_2O_3, SiO_2 and Nb_2O_5, brought about high activities. The temperature to show the 30% conversion on the latter oxides was lower than that on the former oxides by 70 K. It is expected that the acid or base property of supports induced a change in surface oxidation state of Pd through an electronic interaction between Pd and support surface, so that the combustion activity changed.

3.2. Affinity for oxygen and reaction order on oxygen pressure

The pretreatment for XPS analysis and the measurement of reaction order were conducted under conditions different from that for the actual catalytic reaction in figure 1; a low oxygen pressure or low reaction temperature was applied on the catalyst. This is necessary for the purpose to determine the affinity of the Pd surface for oxygen, since it is supposed that Pd oxide would occupy all over the Pd surface under such high pressure of oxygen as 20 kPa or the high reaction temperature above 650 K. Whereas under the appropriate condition, it becomes possible to observe the alternation in Pd surface composition according to the change in acid or base property of metal oxides.

Figure 2 shows the XPS Pd 3d of Pd supported on various oxides measured after pretreatment at 573 K under the oxygen flow. Dotted lines are peak positions which correspond to the metal Pd or PdO [10]. Whereas the metal Pd phase prevailed on Pd/MgO, the peak position shifted towards higher binding energy with increase in the acid property of support, and it became close to the position of PdO in Pd/WO_3. Exceptionally, the oxidation state of Pd on SiO_2 deviates from the above tendency, where metal Pd phase was abundant in spite of its neutral acid–base property. The relationship between maximum Pd $3d_{5/2}$ peak position and the electronegativity of the metal cation of the

Table 1
Surface area and dispersion of Pd for Pd loaded on various metal oxides.

	Pd/MgO	Pd/Al_2O_3	Pd/SiO_2	Pd/Nb_2O_5	Pd/WO_3
Surface area ($m^2\ g^{-1}$)	15.7	10.4	41.8	11.4	10.3
Dispersion (%)	14.1	4.1	21.5	3.6	3.1

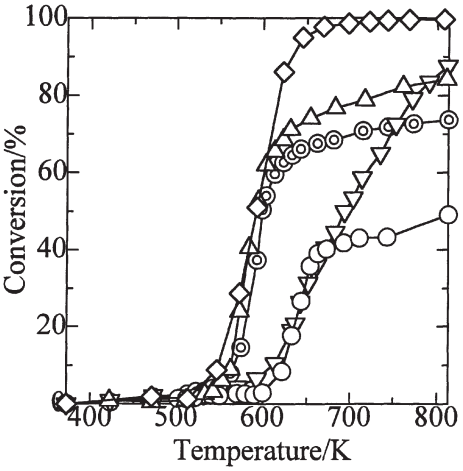

Figure 1. Catalytic combustion of toluene over Pd loaded on various metal oxides: (○) MgO, (△) Al_2O_3, (◇) SiO_2, (◎) Nb_2O_5, and (▽) WO_3.

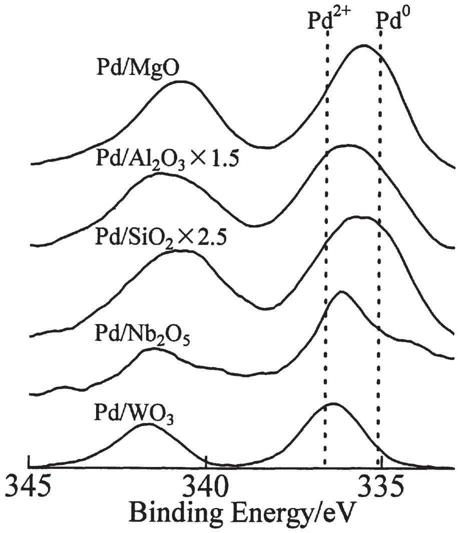

Figure 2. XPS Pd 3d of Pd supported on various oxides after calcination under oxygen flow at 573 K.

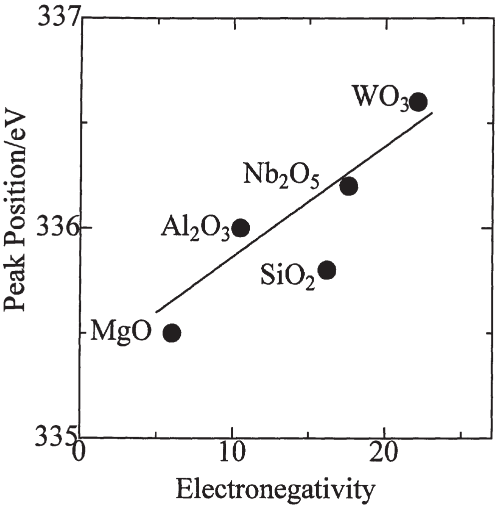

Figure 3. Correlation of maximum Pd $3d_{5/2}$ peak position and electronegativity of metal cation of the support metal oxide.

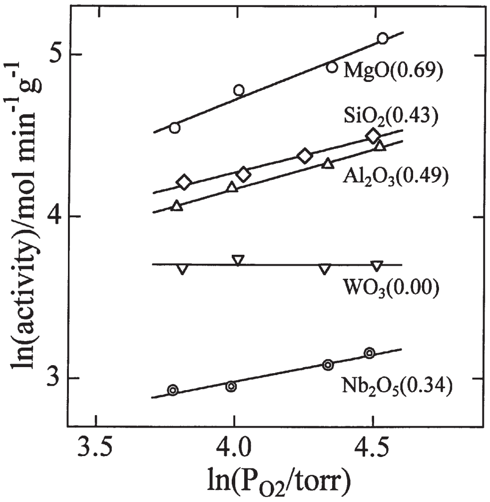

Figure 4. Dependence of combustion activity of toluene on the oxygen pressure: (○) MgO at 658 K, (△) Al_2O_3 at 593 K, (◊) SiO_2 at 658 K, (◎) Nb_2O_5 at 593 K, and (▽) WO_3 at 673 K.

support oxide was plotted in figure 3. The electronegativity was regarded as an indication of acid or base property of the metal oxide. A linear relationship was obtained between these two factors, though Pd/SiO_2 deviates somewhat from this line. This means that the surface of Pd is easily oxidized, when Pd is supported on the acidic support, whereas metal Pd is stabilized on the basic support. This observation can be explained by the electronic character of support, which is related with the acid–base property of metal oxide. Acidic support with electrophilic character results in the electron-deficient state of Pd, thus the Pd surface is easily oxidized to generate the surface PdO. On the other hand, basic support with electrophobic character makes the Pd particle electron-sufficient, thus the Pd surface becomes difficult to be oxidized. Probably exceptional behavior of Pd/SiO_2 came from the weak interaction between SiO_2 surface and Pd. As described above, the combustion activity over the Pd on a metal oxide with weak acid or base property was higher than that on a strong acid or base one. Taking the above results into account, two possibilities can be indicated for the active phase of Pd. One is the co-existence of Pd and PdO over the Pd surface, where metal Pd act as adsorption sites for hydrocarbon molecule. The adsorbed molecule diffuses to the PdO region and is oxidized to carbon dioxide and water. Another possibility is that, on the neutral oxide support, the bond strength of oxygen and surface Pd is optimized for the combustion of toluene.

To obtain further knowledge about the oxidation state of Pd surface, the reaction order on the oxygen pressure was measured, under the toluene pressure of 1.0 kPa. Figure 4 shows the dependence of activity on the oxygen pressure. The reaction order agreed well with the change in acid–base property of support, i.e., MgO(0.69) > Al_2O_3(0.49) > SiO_2(0.43) > Nb_2O_5(0.34) > WO_3(0.00). The result can be explained by the observation in the XPS experiment. On the extremely acidic support, the change in oxygen pressure has no effect on the combustion activity, because PdO predominates over Pd surface. On the other hand, metal Pd phase is abundant on the basic support, thus the reaction order had a significant value. Although the reaction order followed the order of acid–base property of metal oxides, the above explanation might not be applicable on Pd/SiO_2, because the exceptional behavior was observed in the XPS study on Pd/SiO_2 where metal Pd was abundant. Indeed, SiO_2 showed a different tendency when other hydrocarbon was used for the reaction, i.e., for the combustion of methane, Pd/SiO_2 showed extraordinary higher activity than other catalysts. As stated above, under the high oxygen pressure at 20.3 kPa, the order was zero for every catalyst. Therefore, it is expected that under the practical conditions of catalytic combustion, almost all of the Pd surface was covered with PdO. However, the participation of metal Pd phase created by the reduction of PdO with toluene molecule cannot be excluded, since it was reported that only a small portion of metal Pd in PdO highly accelerated the combustion of Pd [1].

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