Catalysis Letters 12 (1992) 287–296

Mechanism of sulfur poisoning on supported noble metal catalyst — the adsorption and transformation of sulfur on palladium catalysts with different supports

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A series of supported palladium catalysts (Pd/Al_2O_3, Pd/MgO and Pd/TiO_2) were prepared by the impregnating method and treated with H_2S, H_2+O_2 or O_2, among which H_2S is used as a poison and H_2+O_2 or O_2 are as purging atmospheres. The S^{2-} species in the supports was introduced by means of mechanically mixing Na_2S with the supports or catalysts. X-ray photoelectron spectroscopy (XPS) was employed to determine the changes in the chemical states of oxygen, palladium and sulfur in the catalysts before and after the treatment, while infrared (IR) spectroscopy was used to measure the SO_4^{2-} group produced in the catalysts and supports. The results show that on MgO and TiO_2 carriers whose acidities are weak, there exist two kinds of oxygen species, one is the lattice oxygen, the other one is the active species of oxygen. The latter can oxidize the S^{2-} into SO_4^{2-} even at room temperature in air. Because of the weak acidities and smaller specific surface area of MgO and TiO_2, the S^{2-} is liable to adsorb on the catalysts and to transform into SO_4^{2-}. But for the case of Al_2O_3 support its acidity is rather strong, and its surface oxygen species under the experimental conditions is not so active as that in MgO and TiO_2 carries. The poison H_2S on the Al_2O_3 support only experiences a process of physical adsorption-desorption. In Pd/Al_2O_3 catalyst, the negatively charged sulfur ions are not so easily adsorbed and transformed as those in Pd/MgO and Pd/TiO_2. It is also implied that the properties of the carriers are related to the ability of self-regeneration of the corresponding catalysts. Pd/Al_2O_3 catalyst is more able to self-regenerate than Pd/MgO and Pd/TiO_2 catalyst.

Keywords: Adsorption and transformation of sulfur; supported palladium catalysts; active oxygen species; self-regeneration

1. Introduction

In our previous works [1–4], the mechanism of sulfur-poisoning on supported noble metal catalysts and the influence of acidity of the supports on sulfur-resistance of the catalysts were studied. It was shown that sulfur-metal bonding is the essential factor leading to the deactivation of supported metal catalysts. However, in practical catalytic process, sulfur can adsorb on both metals and the supports. Works [5,6] about the effect of sulfur adsorption on the supports upon the characters of the catalysts have hardly been seen yet. In this study, a series of model supported palladium catalysts have been prepared. S^{2-} species was introduced by physically mixing Na_2S with the catalysts instead of direct adsorption of H_2S. In this way, the noble metals on the supports are expected to have little direct interaction with S^{2-}. The S^{2-} species in these samples therefore is equivalent to that in the supports. The catalysts were then studied with spectroscopic methods after various treatments. XPS was applied to determine the chemical states of sulfur, oxygen and palladium. IRS was used to analyze the binding environment of sulfur in the catalysts. The results show that the influence of sulfur on the supported noble metal catalysts was different owing to the properties of the various supports and a sulfur poisoning mechanism of the catalysts was further discussed.

2. Experiment

1. CATALYSTS PREPARATION

Pd/Al_2O_3, Pd/MgO and Pd/TiO_2 (5 wt% Pd) were prepared by impregnation. The detailed procedure was described in ref. [4].

2. INTRODUCTION OF S^{2-} SPECIES

One way is physically mixing Na_2S with the reduced catalysts or supports, ground up evenly and dried in vacuum at 130°C. The amount of S^{2-} species in the sample is 5 wt%. Another way is treating the catalysts or supports with a mixed stream of $H_2S + H_2$ (H_2S, 15% in volume) at 130°C for 20 min, then cooled to room temperature in the atmosphere.

3. XPS MEASUREMENTS

Using MgK_α ($h\gamma = 1253.6$ eV) as an exited source, the XPS spectra were recorded on the ESCA-LAB MKII machine. The sample was pressed into self-supported wafers and degassed in a pretreatment chamber. The experimental data were referred to contaminative carbon (C1s, 284.6 eV).

4. IR ANALYSIS

This was carried out on a Perkin-Elmer FTIR-1800 infrared spectroscopy photometer. The characteristic frequency of the SO_4^{2-} group in the catalyst within the range of 1040 cm^{-1} to 1210 cm^{-1} was checked.

3. Results and discussion

1. THE ACTIVE OXYGEN SPECIES

XPS measurements of ground physical mixture of TiO_2, MgO and Al_2O_3 with Na_2S display different states of oxygen. Only one state of the lattice oxygen prevails on the γ-Al_2O_3 carrier (O1s, 531.6 eV). On MgO and TiO_2, however, there are two kinds of oxygen state (O1s for MgO, 531.1 eV and 529.6 eV; for TiO_2, 530.9 eV and 528.9 eV, fig. 2). The oxygen species with a lower binding energy is assigned to the lattice oxygen in the supports (TiO_2 and MgO), and that with a higher binding energy must be the active adsorbed oxygen species in the form of OH^- [7]. These spectra shown in fig. 1 are identical with those on the corresponding pure supports [8]. This demonstrates that Na_2S in the physical mixtures has no detectable effect on the intrinsic nature of the supports.

Owing to the high oxidative ability of adsorbed OH^- under mild condition (for example in air at room temperature), S^{2-} ion can be oxidized into SO_4^{2-} group on MgO and TiO_2, so S^{6+} species is checked in MgO and TiO_2 after they are mixed with Na_2S (fig. 2). S^{2-} remains as in Na_2S in the mixture of Al_2O_3 and Na_2S (fig. 2-1). IR results are in accordance with those of XPS (fig. 3-1, 2, 3). On Al_2O_3 mixed with Na_2S, SO_4^{2-} absorption is absent in the IR spectrum, while the characteristic bands of SO_4^{2-} (1104 cm^{-1}) are apparent for MgO and TiO_2 supports containing Na_2S. This also gives some evidence of the strong oxidative ability of MgO and TiO_2. Obviously, this ability comes from the active oxygen species in the supports.

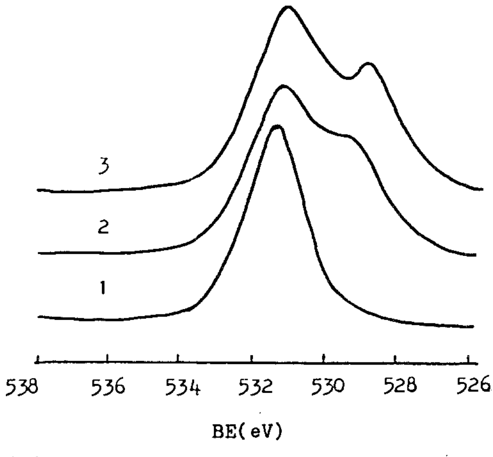

Fig. 1. XPS spectra of O(1s) for different catalysts mixed with Na_2S in air. 1: Al_2O_3, 2: MgO, 3: TiO_2.

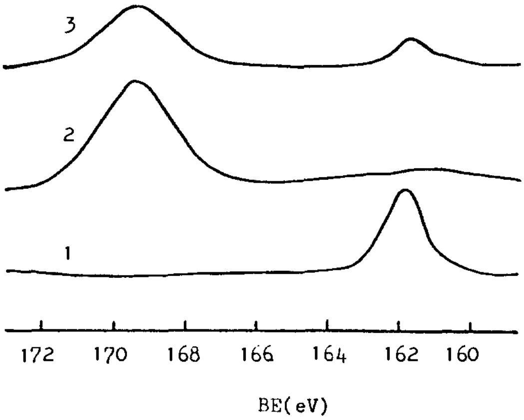

Fig. 2. XPS spectra of S(2p) for different supports mixed with Na_2S in air. 1: Al_2O_3, 2: MgO, 3: TiO_2.

2. THE CHEMICAL STATES OF PALLADIUM ON DIFFERENT CARRIERS

The properties of supported palladium vary with different supports (fig. 4). On Pd/Al_2O_3 catalyst, palladium exists in two states, i.e. 335.5 eV and 334.8 eV for Pd $3d_{5/2}$. On MgO and TiO_2 supports, XPS reveals only one state of Pd

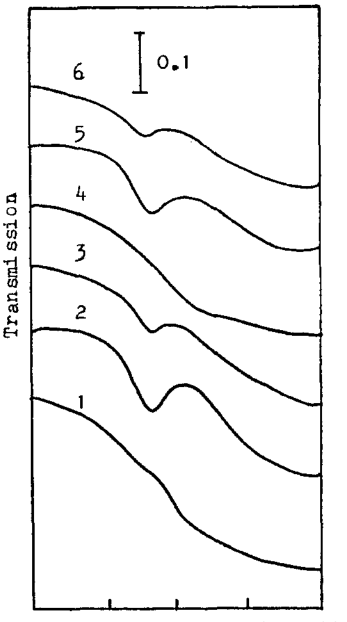

Fig. 3. IR spectra of different catalysts mixed with Na_2S in air. 1: Al_2O_3, 2: MgO, 3: TiO_2, 4: Pd/Al_2O_3, 5: Pd/MgO, 6: Pd/TiO_2.

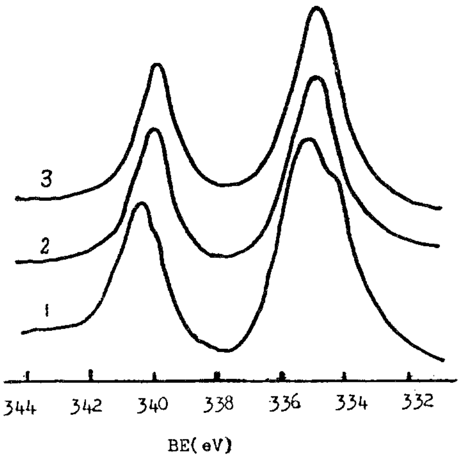

Fig. 4. XPS spectra of Pd(3d) for different catalysts. 1: Pd/Al_2O_3, 2: Pd/MgO, 3: Pd/TiO_2.

(Pd $3d_{5/2}$, 334.8 eV). The difference of Al_2O_3 from MgO and TiO_2 is due to the fairly strong acidic sites on Al_2O_3 compared with MgO and TiO_2. Those palladium particles located at these sites are electron deficient and therefore display a higher binding energy (335.5 eV). These palladinum particles located far away from the acidic sites are subjected to a weak effect and display a lower binding energy (334.8 eV). On the surface of TiO_2 and MgO which possess smaller specific surface area and a little basicity, the precious metal is little influenced by the supports, so it shows the electronic nature of the pure metal. The physical properties of these supports are listed in table 1.

3. The influence of sulfur in the supports on the performance of the catalysts

The results of XPS spectra for sulfur (fig. 5) in the catalysts show that sulfur on the sample ($Pd/Al_2O_3 + Na_2S$) is in S^{2-} form. As mentioned before, the S^{2-} does not combine with the palladium directly and is in the form of Na_2S. For the ($Pd/MgO + Na_2S$) sample, the dominant sulfur is in the S^{6+} state. It means that during mixing Na_2S with the catalyst, S^{2-} is oxidized into the SO_4^{2-} group. On Pd/TiO_2 with Na_2S, not only S^{2-}, but also SO_4^{2-} are presented. IR

Table 1
Physical properties of the supports

Supports	Al_2O_3	TiO_2	MgO
S_{BET} (M^2/g)	220.2	9.1	35.5
The amount of NH_3 adsorbed (arb. unit)	36.0	5.0	0.4

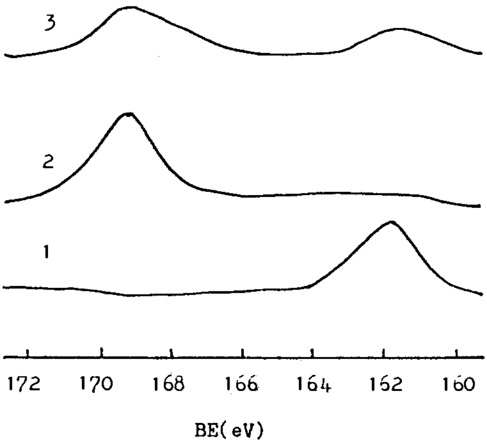

Fig. 5. XPS spectra of S(2p) for catalysts mixed with Na_2S in air. 1: Pd/Al_2O_3, 2: Pd/MgO, 3: Pd/TiO_2.

analysis (fig. 3-4, 5, 6) displays that the SO_4^{2-} group was formed on ($Pd/TiO_2 + Na_2S$) and ($Pd/MgO + Na_2S$). However, on the ($Pd/Al_2O_3 + Na_2S$) sample, no SO_4^{2-} group was checked out. This is consistent with the results of XPS.

On the basis of the above results, it is pointed out that S^{2-} species existing in various carriers affect the catalysts differently. In Pd/Al_2O_3 catalyst, S^{2-} cannot be converted into SO_4^{2-}, while on Pd/TiO_2 and Pd/MgO catalysts, there exists active oxygen species and S^{2-} species is easily transformed into SO_4^{2-} and then accumulates on it. Because the life of the catalyst in H_2-O_2 reaction is closely related to the amount of SO_4^{2-} in the catalyst when sulfur is the main poison [1,4], so the S^{2-} in supports of TiO_2 and MgO can shorten the life of Pd/MgO and Pd/TiO_2 to some extent.

4. THE INFLUENCE OF DIFFERENT SUPPORTS ON THE ABILITY OF “SELF-REGENERATION” OF THE CATALYSTS

Fig. 6 shows the results of XPS for Pd 3d on Pd/MgO, Pd/TiO_2 and Pd/Al_2O_3 catalysts pretreated with H_2S at 130°C for 10 min. It can be seen that after the catalysts are purged with mixed gas of ($H_3S + H_2$), oxidized and metallic palladium are present. The only difference is in that the relative amount of various states is distinct. On Pd/TiO_2 and Pd/MgO catalyst, there is a little more oxidative metal than on Pd/Al_2O_3. When these presulfurized catalysts are treated with pure oxygen at 200°C, the binding energy of Pd $3d_{5/2}$ in Pd/Al_2O_3 shifts a little higher (fig. 7-1), but a large change (by 1.2 eV increase) in Pd/MgO and Pd/TiO_2. This is attributed to the active oxygen species on the supports which can oxidize PdS and Pd^0 into oxidative state (PdO).

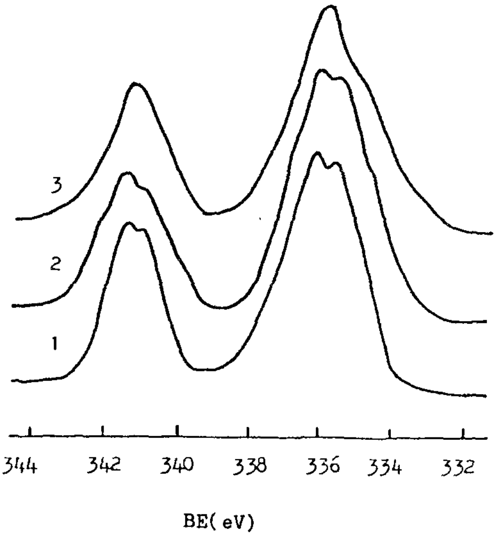

Fig. 6. XPS spectra of Pd(3d) for catalysts treated with H_2S at 120°C. 1: Pd/Al_2O_3, 2: Pd/MgO, 3: Pd/TiO_2.

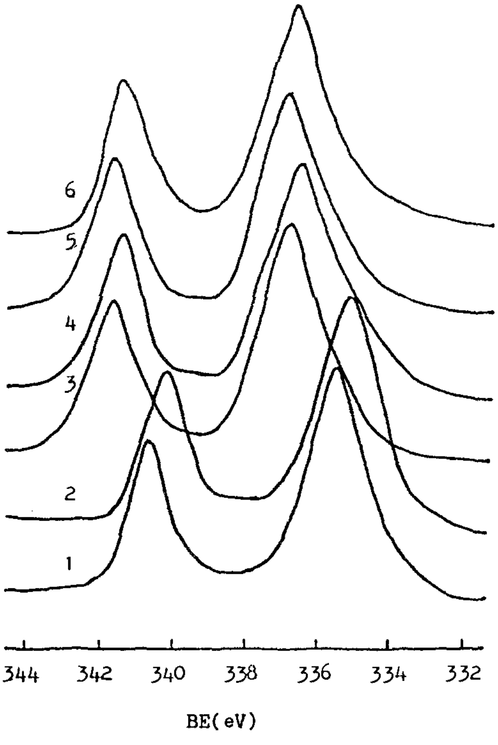

Fig. 7. XPS spectra of Pd(3d) for presulfurized catalysts treated with different atmosphere at 200°C. 1-2: Pd/Al_2O_3, 3-4: Pd/MgO, 5-6: Pd/TiO_2. 1-3-5: catalysts treated with O_2. 2-4-6: catalysts treated with $H_2 + O_2 + Ar$.

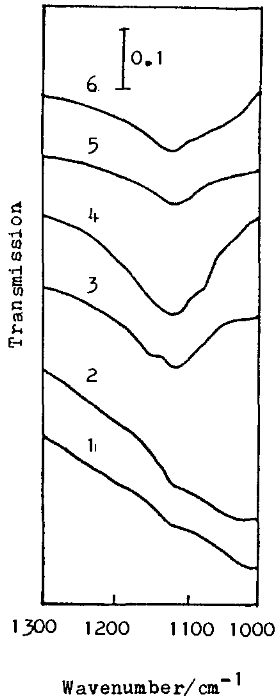

Fig. 8. IR spectra of catalysts treated with different atmosphere at 200°C. 1-2: Pd/Al_2O_3, 3-4: Pd/MgO, 5-6: Pd/TiO_2. 1-3-5: treated with O_2, 2-4-6: treated with H_2+O_2+Ar.

IR analysis for presulfurized catalysts treated with pure oxygen at 200°C shows that only a little SO_4^{2-} is found in Pd/Al_2O_3 while a lot of SO_4^{2-} is produced in Pd/TiO_2 and Pd/MgO catalysts. The reason for these results must be: 1. The rate of S^{2-} converted into SO_4^{2-} is slow on Pd/Al_2O_3 catalyst, but fast and easily on Pd/MgO and Pd/TiO_2, whose supports have active oxygen species. 2. The relatively strong acidity of Al_2O_3 depresses the adsorption of S^{2-} on Pd/Al_2O_3. However, TiO_2 and MgO have a weak acidity. During the oxidation of S^{2-}, palladium in the catalysts is oxidized at the same time. The process is expressed as following eq. (2) below.

When the presulfurized catalysts are treated with the mixture stream of H_2+O_2+Ar ($H_2:O_2=1:1$, H_2, 5% in volume) at 200°C for 10 min, IR analysis (fig. 8-2, 4, 6) demonstrates that the amount of SO_4^{2-} formed on Pd/Al_2O_3 catalyst is still less than that on Pd/MgO and Pd/TiO_2 catalysts. The reason is similar to that of the catalyst treated with pure oxygen. But the XPS measurements for active components show a large difference among them (fig. 7-2, 4, 6). The palladium on presulfurized Pd/Al_2O_3 catalysts treated with H_2+O_2+Ar exists primarily in Pd^0 state, the noble metal remains its active state. After presulfurized Pd/TiO_2 and Pd/MgO catalysts are treated with H_2+O_2+Ar, palladium in oxidative state (Pd $3d_{5/2}$, 336.4 eV), their activities restore less than that of the presulfurized Pd/Al_2O_3 catalyst after similar treatment.

According to our previous experimental results [2–4], the following reactions happened on the catalysts during the sulfur poisoning in H_2-O_2 catalytic reaction. The process is called “self-regeneration”.

$$\mathrm{Pd/support} + \mathrm{H_2S} – \mathrm{Pd}x\mathrm{S/support} + \mathrm{H_2}\ (0.5 < x < 4) \tag{1}$$

$$\mathrm{Pd}x\mathrm{S/support} \xrightarrow[\mathrm{Pd}]{\mathrm{H_2O,\ O_2}} \mathrm{PdO/support} + (\mathrm{H_2O} + \mathrm{SO_3}) \tag{2}$$

$$\mathrm{PdO/support} \xrightarrow[200^{\circ}\mathrm{C}]{\mathrm{H_2}} \mathrm{Pd/support} + \mathrm{H_2O}. \tag{3}$$

It is postulated that when sulfur-poisoned Pd/Al_2O_3 catalyst is treated with $H_2 + O_2 + Ar$, reaction (3) takes place easily, so it has a higher ability of “self-regeneration”. While on Pd/MgO and Pd/TiO_2 catalysts, S^{2-} is converted into SO_4^{2-} and accumulates in the support, it is not fast enough to reduce the oxidized palladium to the metal, i.e. reaction (2) goes on quickly and reaction (3) is relatively slow, so they have lower ability of “self-regeneration”.

4. Conclusion

1. The adsorption properties of S^{2-} species on supported palladium catalysts differ from each other with the supports. There is scarcely active oxygen species in Al_2O_3 support, so the behavior of S^{2-} on it seems to be in a process of physical adsorption-desorption. The SO_4^{2-} in Pd/Al_2O_3 comes mainly from the S^{2-} bonded with palladium catalytically being oxidized into SO_4^{2-}, some of which diffuses into the supports. The S^{2-} in TiO_2 and MgO supports which possess active oxygen species is liable to be converted into SO_4^{2-}, that is to say, the S^{2-} is not only adsorbed, but also reacts with the active oxygen species. Thus for Pd/MgO and Pd/TiO_2 catalysts, except that some SO_4^{2-} is produced in the same way as in Pd/Al_2O_3 mentioned above, the dominant SO_4^{2-} results from the S^{2-} adsorbed directly being oxidized by the active oxygen species of the supports.

2. The nature of the supports has some effect upon the ability to adsorb and transform the S^{2-} species. Al_2O_3 support with a fairly stronger acidity makes S^{2-} more difficult to adsorb on Pd/Al_2O_3 catalyst, but on Pd/TiO_2 and Pd/MgO catalysts, whose supports have a little stronger basicity and active oxygen species, S^{2-} is easy to adsorb on them and to transform into SO_4^{2-} group that has less toxity in a definite scope.

3. The palladium catalysts with different supports have different ability of “self-regeneration”. Pd/Al_2O_3 catalyst has rather high ability to self-regenerate relative to Pd/MgO and Pd/TiO_2 catalysts.

Acknowledgements

We thank the National Natural Science Foundation of China for financial support. The Dalian National Lab. for Catalysis in acknowledged for the experimental association and partial financial support. We are also indebted to professor Guo Xiexian, Xin Qin, Jiang Zhicheng and Dr. Li Can for helpful advice and discussion.

References

[1] An Lidun and Deng Youquan, Appl. Catal. 66 (1990) 219.
[2] Pang Xinmei, An Lidun and Ma Jun, Hua Xue Tong Bao (Chemistry) 11 (1990) 42 (China).
[3] An Lidun, Deng Youquan, Xiao Tiancun, ma Jun and Xu Hongbin, Abstract Proc. 5th National Symp. Catal., Lanzhou, August, 1990, p. 765.
[4] Xiao Tiancun, Master Thesis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, July 1990.
[5] C.R. Apesteguia, S.M. Trevizen, T.F. Gartto and J.F. Plaza, React. Kinet. Catal. Lett. 20 (1982) 1.
[6] M. Guenin, M. Breysse, R. Frety, K. Tifouti, P. Marecot and J. Barbier, J. Catal. 105 (1988) 144.
[7] S.R. Morrison, *The Chemical Physics of Surface* (Plenum Press, New York and London, 1977).
[8] A. de Mallmann, Stud. Surf. Sci. Catal. 46 (1988) 429.