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# Dehydrogenative Coupling of Methane Catalyzed by Platinum-Added Sulfated Zirconia and Characterization of the Catalyst Surface

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**An active and stable catalyst of 3 wt% Pt-added sulfated-zirconia for the dehydrogenative coupling of methane without oxidant was obtained by sulfating zirconia gel with 0.5 *M* $H_2SO_4$, followed by drying, impregnating the sulfated gel with a solution of $H_2PtCl_6$, calcining in air at 600°C, and finally reducing in $H_2$ at 500°C. The catalyst gave conversion of 0.23%, ca 40% of the equilibrium value, at 500°C and was steady during the run of 5 h in a flow reactor (0.5 g catalyst, 10 ml/min methane). The products were ethane and ethylene in a ratio of 9 : 1; $CO_2$ was negligible. A remarkable loss of activity was observed with the catalysts sulfated with ammonium sulfate instead of sulfuric acid. XRD analysis showed that the sulfation of zirconia gel with sulfuric acid led to high dispersion of the Pt matter onto the support; the observations were confirmed by the amount of CO chemisorbed on the surface Pt atom. The adsorption measurement of CO showed the ratio of CO/Pt to be 0.09. Using TG-DTA the sulfur quantity on the catalyst was estimated from a weight loss at 600–1000°C, caused by decomposition of the sulfate species, and the ratio of Pt to S was determined to be 1. XPS showed $SO_4^{2-}$ for the S state and 10% of the platinate to be in the metallic state. Measurements of TG-DTA and XPS, in addition to the CO chemisorption, showed an active site (in the steady state) to be $Pt^0$-$SO_4/ZrO_2$, surrounded by 10 times platinate-$SO_4/ZrO_2$ with various oxidation numbers of Pt except 0, whose species protect the active one from aggregation. The turnover frequencies were estimated to be 0.18 $min^{-1}$.** © 1998 Academic Press

## INTRODUCTION

The partial oxidation of methane to form $C_2$ and higher hydrocarbons is an alternative to petrochemical feedstocks. A number of catalytic systems that show methane conversions and $C_2$ hydrocarbon selectivities have been reported (1–6), several reviews being also found (7–9). The mechanism for this reaction is believed to initiate the homolytic cleavage of a C-H bond, resulting in the formation of $CH_3$ radicals which undergo coupling to form ethane; therefore hydrogen atom abstraction becomes a critical step in the activation process. The reaction usually needs high temperatures, more than 700°C.

Work in our laboratory has demonstrated that on the oxide surfaces of Fe, Ti, Zr, Hf, Sn, Si, and Al superacids with an acid stronger than that of 100% $H_2SO_4$ are generated by addition of the sulfate species. Solid acids with an acid strength of up to the Hammett acidity function Ho below −16.04 were synthesized by adsorbing sulfate ion onto the amorphous oxides followed by calcination in air above 500°C (10–12). The superacids were active in a heterogeneous system for reactions of hydrocarbons such as butanes and pentanes.

We have also demonstrated that impregnation of the sulfated zirconia ($SO_4/ZrO_2$) with Fe, as well as noble metals such as Pt and Pd, leads to pronounced activity for the reaction of butane to isobutane, much more active than the $SO_4/ZrO_2$ and the highest in acidity among the superacids prepared by the addition of sulfate ion to metal oxides, the Pt concentration being 7–8 wt%; the catalyst with Pt was highest in activity for the reaction, more active than any solid catalyst yet reported (13–15).

We also studied the zirconia-based catalysts for the reaction of methane; sodium doped $ZrO_2$ was found to be active for the selective formation of $C_3$ hydrocarbons at the relatively low temperature range, ≤600°C (16), and organic compounds containing oxygen, mainly acetaldehyde, were formed over $SO_4/ZrO_2$ (17). Following these observations, application of the noble metal-doped $SO_4/ZrO_2$ to methane activation is now of interest. In the present paper we report the selective coupling of methane to ethane over Pt-$SO_4/ZrO_2$ without using $O_2$ as the oxidant.

## EXPERIMENTAL

First zirconia gel was obtained by hydrolyzing $ZrOCl_2$ with aqueous ammonia to pH 8 at a temperature of 50–60°C; aqueous ammonia solution (25%, ∼15 ml) was added dropwise with stirring into 25 g of $ZrOCl_2 \cdot 8H_2O$ dissolved in 500 ml of distilled hot water, followed by keeping the precipitated solution in a water bath warmed at 50–60°C for 6 h, washing the precipitate 2–3 times with 250 ml of hot water for each, and drying at 110°C for a yield of 10 g.

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### *Pt-$SO_4/ZrO_2$(S)*

Two grams of the gel (20–30 mesh) were immersed in 30 ml of 0.5 *M* $H_2SO_4$ for 0.5 h, followed by filtering and drying at 100°C for 1 h. The resulting sulfated gel was impregnated with 7 ml of aqueous $H_2PtCl_6 \cdot 6H_2O$ (to obtain 1, 3, 5, and 7.5 wt% Pt in the final catalyst), followed by evaporating the residual water, drying, and finally calcining in air at 600°C for 3 h.

### *Pt-$SO_4/ZrO_2$(A)*

Four grams of the gel were impregnated with 7 ml of aqueous $H_2PtCl_6 \cdot 6H_2O$, followed by evaporating the water and drying; the Pt quantity was 1, 3, 5, and 7.5 wt% based on Pt-$ZrO_2$. The dried Pt-doped gel was then kneaded well with ammonium sulfate using a mortar and pestle; the quantity of $(NH_4)_2SO_4$ was 15 wt% (3.6 wt% S) based on Pt-$ZrO_2$. The kneaded material (20–30 mesh) was preheated at 150°C for 1.5 h and calcined at 600°C for 3 h (13).

### *Pt-$ZrO_2$*

Platinum-added zirconia without the sulfation was prepared by impregnation of the gel with the aqueous platinate following the above procedures: 3 wt% Pt and 600°C, 3 h for calcination.

The coupling of methane (research grade) was carried out at atmospheric pressure in a single-pass fixed-bed Pyrex reactor; 0.5 g of catalyst powder (20–30 mesh) was placed between glass wool plugs. The reduction of catalyst was performed in hydrogen at a flow rate of 10 ml/min at 500°C for 1 h before reaction. After the pretreatment methane was introduced at a rate of 10 ml/min without any carrier gas, and effluent products were analyzed with an on-line gas chromatograph (Porapack R-2 m, 30°C). Calculation of the low conversion of methane was based on the appearance of products; the GC system used detected all the products.

The amount of surface Pt atoms was measured volumetrically by CO chemisorption at room temperature on samples reduced in hydrogen. A conventional pulse reactor with a fixed-bed catalyst, equipped with calibrated bulbs, was used for the volumetric measurements. After a 0.5 g sample (0.3 g after the reaction of methane) was heated in flowing hydrogen (10 ml/min) at 500°C for 1 h and cooled to room temperature, CO was adsorbed passing through the sample bed several times while the remaining amount of CO was monitored with the gas chromatograph. When the g.c. area reached a steady point the amount of CO adsorbed was quantified by comparing the area under the TCD curve to peak areas of CO calibration pulses injected. An adsorption stoichiometry of CO (adsorbed) : Pt (surface atom) = 1 was used in the calculations.

Thermogravimetric and differential thermal analysis (TG-DTA) was carried out using a Rigaku model with an operating range from room temperature to 1000°C at a programmed rate of 10°C/min. X-ray powder diffraction (XRD) spectra were obtained with an X-ray diffractometer (Rigaku RAD-RB) by using Cu radiation (100 mA, 30 kV). Infrared (IR) spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer using a tablet mixed with 2 mg of catalyst and 50 mg of KBr. X-ray photoelectron spectra (XPS) were measured with Ulvac-Phi XPS5600ci using Al K radiation (300 W).

## RESULTS AND DISCUSSION

Much attention has been focused on the oxidative coupling of methane because of the thermodynamically advantageous reaction with $\Delta G = -30$ Kcal/mol at 600°C. However, many kinds of catalyst systems still need high temperatures to get the satisfactory activity and selectivity, 600°C or higher. On the other hand, the dehydrogenative coupling of methane is thermodynamically disadvantageous ($\Delta G = 17$ Kcal/mol at 600°C), but it is one of the attractive catalytic reactions to be developped.

The dehydrogenative reaction without any oxidant was carried out over the Pt-$SO_4/ZrO_2$(S) catalysts after reduction in hydrogen at 500°C. The results with 3 wt% Pt at 500°C are shown in Fig. 1 as a function of time on stream. A steady conversion of 0.2% was observed between 100 and 180 min after a rapid increase of conversion in the first 20 min, and this high conversion was maintained over 360 min. The products were ethane and ethylene in the ratio 9 : 1; no $CO_2$ was detected. Since the equilibrium conversion of methane into ethane and dihydrogen is estimated thermodynamically to be 0.6%, this conversion is satisfactory judging from the reaction temperature of 500°C.

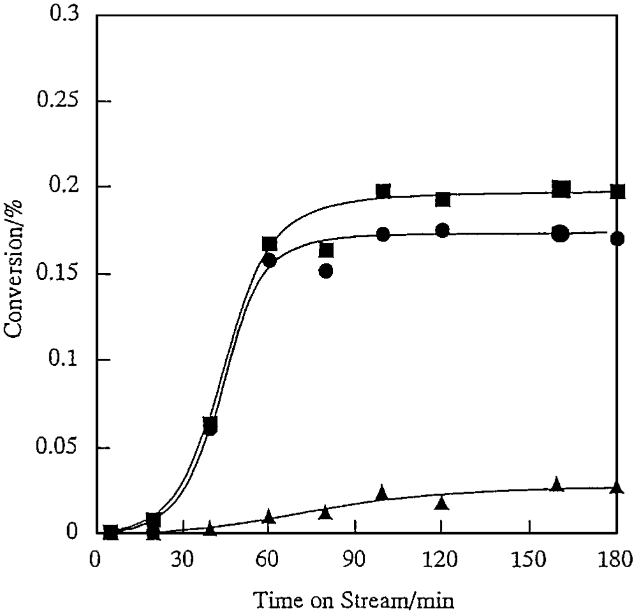

**FIG. 1.** Reaction of methane over 3% Pt-$SO_4/ZrO_2$(S) at 500°C: (■) conversion; (●) ethane; (▲) ethylene.

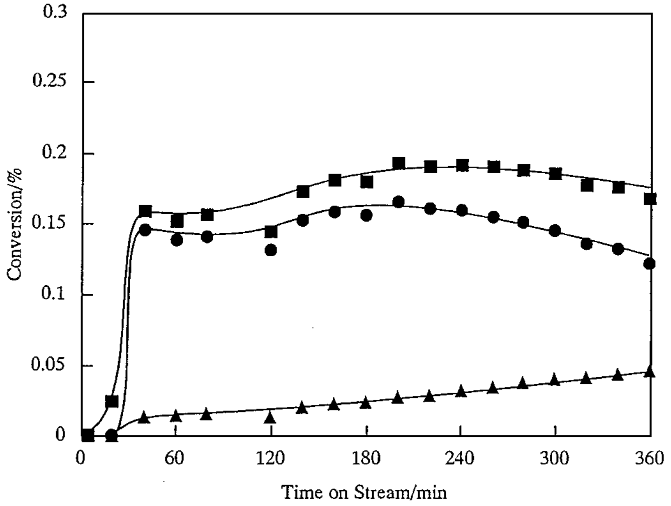

**FIG. 2.** Reaction of methane over 7.5% Pt-$SO_4/ZrO_2$(S) at 500°C: (■) conversion; (●) ethane; (▲) ethylene.

A highly active superacid of $SO_4/ZrO_2$ for the low temperature conversion of butane was obtained by the addition of a large amount of Pt; the maximum activity was observed with 7.5 wt% Pt (based on the gel) (14). Thus, the 7.5% Pt-$SO_4/ZrO_2$(S) catalyst was examined in the reaction, the results for longer time on stream being shown in Fig. 2. No effect on the conversion increase was observed, although the induction period was shorter. The conversion was relatively constant after 180 min, but the product ratio of ethylene/ethane gradually increased with time. It is proposed that loading a large amount of Pt leads to this behavior. It is seen, together with the results in Fig. 1, that this catalyst system is quite steady during the run.

Hydrogen was detected in the products by the negative peak with TCD of detector in the GC chart. When $H_2$ was mixed in the reactant stream, the conversion dropped, owing to the influence of the reverse reaction, while the conversion recovered its normal steady state activity when hydrogen was released. The effect of modifying the period of reduction before reaction by more than 1 h was studied; the catalytic action was not altered, the unit hour being sufficient.

Highly active 7.5% Pt-$SO_4/ZrO_2$ catalyst for the butane conversion was also obtained by sulfation with ammonium sulfate in place of sulfuric acid. Thus, the preparation method was examined; that is, the Zr gel was impregnated with the platinate (7.5 wt% Pt) followed by kneading well with ammonium sulfate, heating at 150°C to melt homogeneously the sulfate, and finally calcining at 600°C, 7.5% Pt-$SO_4/ZrO_2$(A). The matter gave 0.1% conversion at most, and a continual loss of activity was observed with time after 60 min, down to half at 120 min. The catalyst caused a sulfurous odor after the reaction, suggesting desorption of the sulfate species from the catalyst surface.

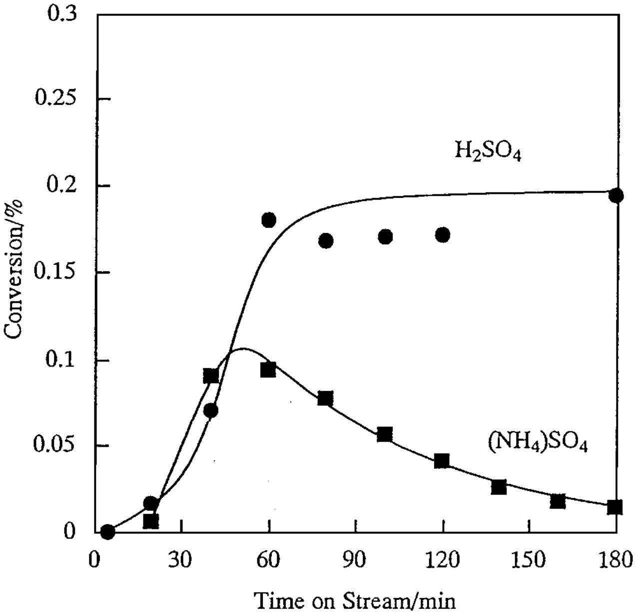

**FIG. 3.** Catalytic activities of 5% Pt-$SO_4/ZrO_2$(S) (●) and 5% Pt-$SO_4/ZrO_2$(A) (■) at 500°C.

The remarkable loss of activity was also observed with 5% Pt-$SO_4/ZrO_2$(A); the results are shown in Fig. 3, together with those of 5% Pt-$SO_4/ZrO_2$(S) for comparison. Figure 3 shows how the sulfation method controls the catalytic activity, as well as the life of the catalyst; the sulfation with sulfuric acid is superior beyond comparison.

Table 1 summarizes the highest activities and the selectivities in several runs over the Pt-$SO_4/ZrO_2$(S) with various quantities of Pt. The maximum conversion, 0.23%, obtained by the materials with 3 and 5% of Pt is ca 40% of the equilibrium value, 0.6%. Although no $CO_2$ was detected in all the runs over the present catalysts, only $CO_2$ was produced when the Pt substance was not loaded. The formation of hydrogen was confirmed in all runs. Analysis of TG-DTA showed carbon deposit on the catalyst to be at most 0.25% of the methane reacted, and the deposition was not concerned with the catalytic activity.

## TABLE 1

**Activities and Turnover Frequencies of Pt-$SO_4/ZrO_2$(S) with Various Amounts of Pt at 500°C**

| Quantity of Pt (wt%) | Conversion (%) | Selectivity (%) | | | TOF ($min^{-1}$) |
|---|---|---|---|---|---|
| | | $C_2H_6$ | $C_2H_4$ | $CO_2$ | |
| 0 | 0.08 | 0 | 0 | 100 | |
| 0[a] | 0.05[a] | 0 | 0 | 100[a] | |
| 1 | 0.12 | 88 | 12 | 0 | 0.16 |
| 3 | 0.23 | 90 | 10 | 0 | 0.18 |
| 5 | 0.23 | 91 | 9 | 0 | 0.16 |
| 7.5 | 0.19 | 90 | 10 | 0 | 0.13 |

[a] Prepared by sulfation with ammonium sulfate.

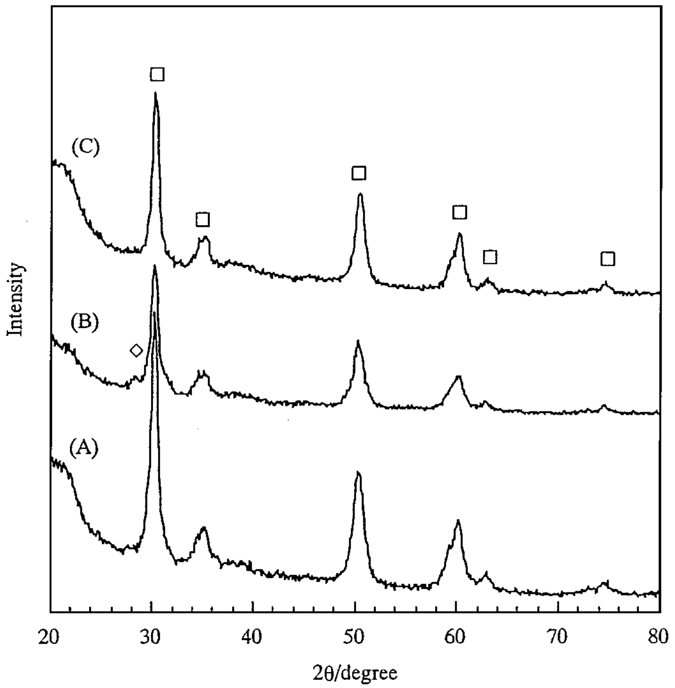

**FIG. 4.** XRD profiles of 3% Pt-$SO_4/ZrO_2$(S) after calcination (A), after reduction (B), and after reaction (C): (□) tetragonal; (◇) monoclinic.

It is indicative that the active site for the coupling is metallic platinum. Thus, Pt-loaded zirconia without the sulfation was examined in the reaction. The 3% Pt-$ZrO_2$ catalyst showed the highest conversion of 0.20% at 60 min, but a large decrease of the conversion, afterward, was observed just like the cases of the catalysts sulfated with ammonium sulfate.

Experiments using XRD were carried out in order to elucidate the surface property of 3% Pt-$SO_4/ZrO_2$(S), whose activity was highest; the spectra are shown in Fig. 4, together with those of the samples before reduction and after reaction for comparison. Zirconium oxide heat-treated at 500°C consists of a mixture of tetragonal and monoclinic forms, and the former converts into the latter form by calcination over 500°C, with only the monoclinic system being developed after calcination over 700°C. The figure shows all of the samples to be 100% tetragonal forms, indicating retardation of the crystallographic phase transformation by sulfation, and no influence on the crystal structure at all is brought about by the reduction nor the reaction.

Although relatively large amounts of platinate were added, any peak based on the Pt substances was not detected (Fig. 4). However, remarkable peaks owing to the Pt metal were found when sulfated with $(NH_4)_2SO_4$ as shown in Fig. 5. The Pt exists on a condensed state, while on a state of dispersion when sulfated with $H_2SO_4$. The results

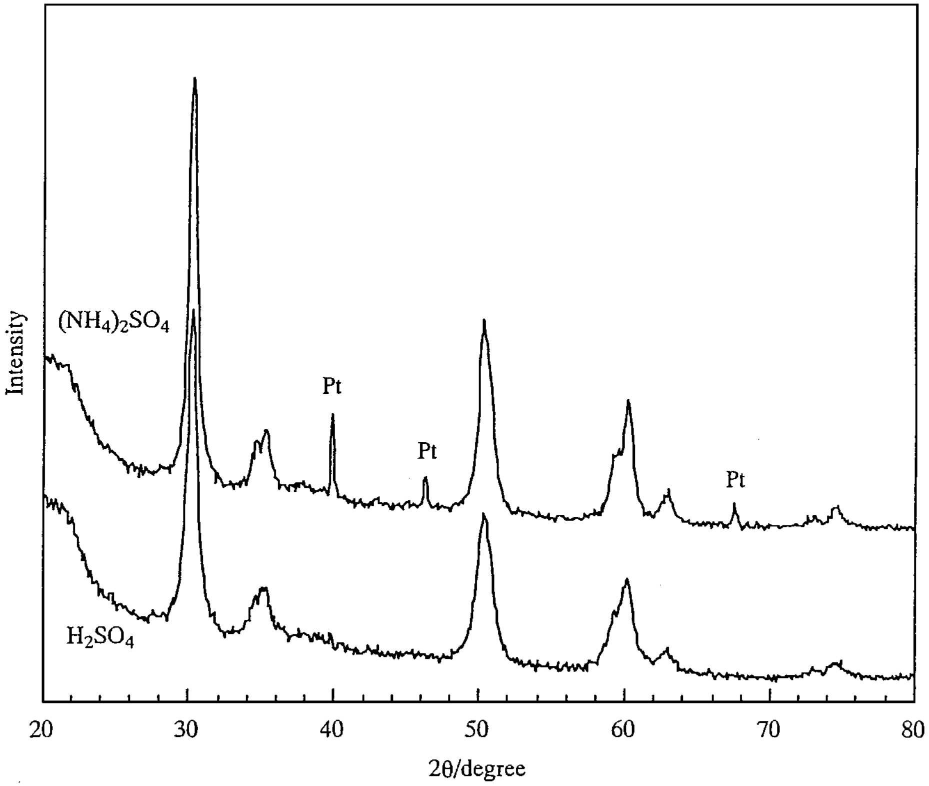

**FIG. 5.** XRD profiles of 3% Pt-$SO_4/ZrO_2$ sulfated with ammonium sulfate and sulfuric acid.

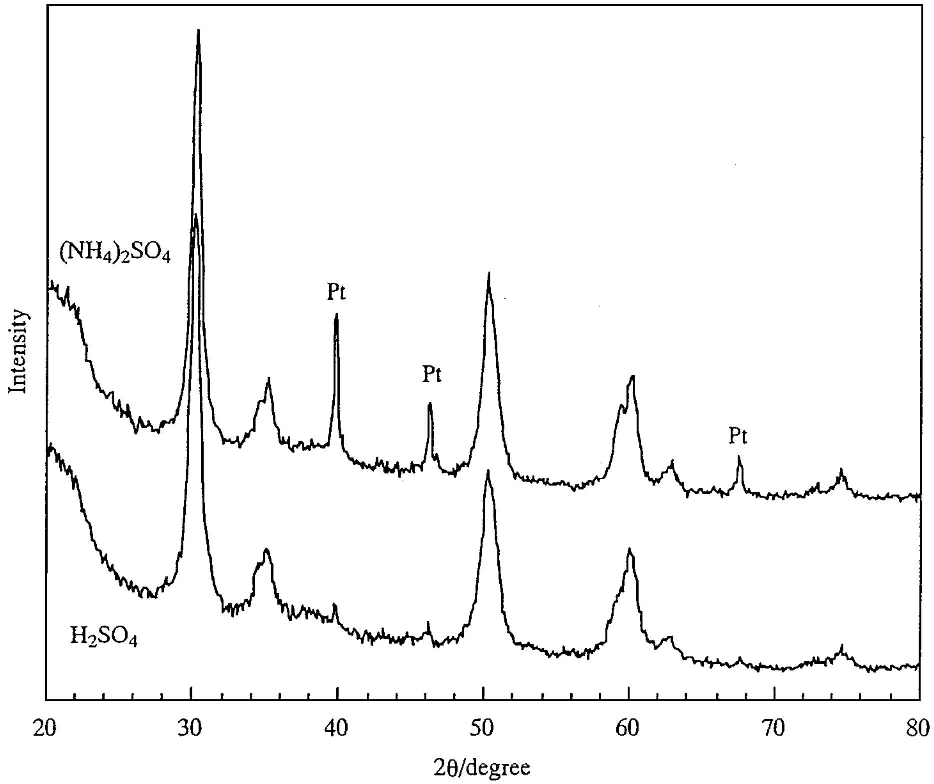

**FIG. 6.** XRD profiles of 7.5% Pt-$SO_4/ZrO_2$ sulfated with ammonium sulfate and sulfuric acid.

show how the sulfation method controls the dispersion of Pt on the catalyst surface. As far as the XRD analysis was concerned, the apparent dispersion was kept at an almost constant state up to the addition of 7.5 wt% of Pt as shown in Fig. 6. It is of interest that impregnating zirconia gel with sulfuric acid leads to quite high dispersion of the Pt matter onto the support.

Relative peak intensities of Pt to $ZrO_2$ using the catalysts after reaction were estimated, and the values are shown in Fig. 7. The estimation was based on the peaks of (111) plane at 30.2 and 39.7° for $ZrO_2$ and Pt, respectively. The peak intensity of Pt for the case of ammonium sulfate increases relatively with the Pt quantity, while not for the case of sulfuric acid, indicating the good dispersion of Pt in the case of the latter.

The dispersion, or fraction of surface Pt atoms, was determined by CO chemisorption. The amount of CO adsorption for the catalysts sulfated with both sulfuric acid and ammonium sulfate, followed by the reduction with $H_2$, was measured as shown in Fig. 8. The amount of CO increased relative to the Pt quantity for the matter sulfated with sulfuric acid, while the volume remained steady as the Pt concentration was increased more than 3% for the cases with ammonium sulfate. The observations are in agreement with those of XRD; the Pt particles begin to grow rapidly as the deposition values exceed 3% for the sulfation with ammonium sulfate.

The adsorption measurement was also performed with the samples with sulfuric acid after reaction (Fig. 8). The results were, however, different from those before reaction; the amount stayed constant from 3 to 7.5% of the Pt

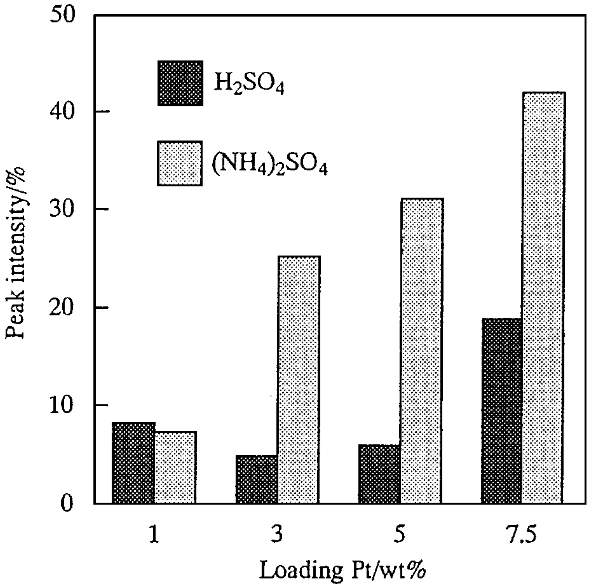

**FIG. 7.** Peak intensity of Pt(111) in the XRD profiles of Pt-$SO_4/ZrO_2$ after reaction.

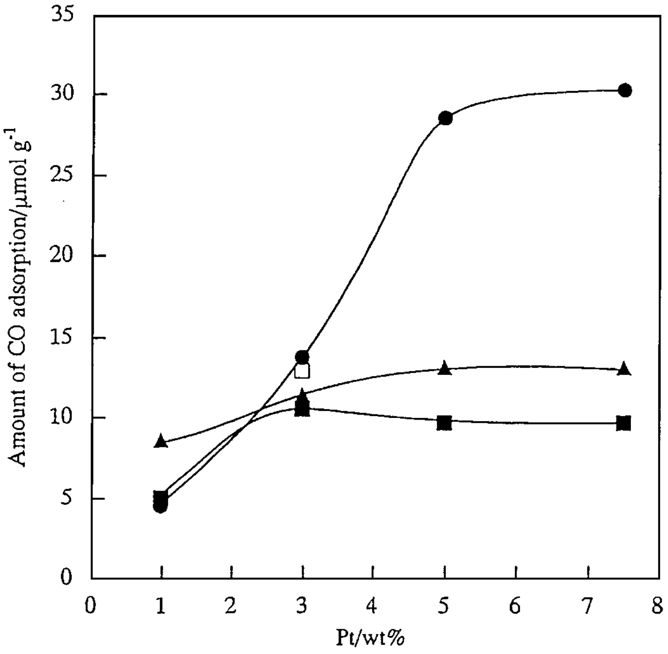

**FIG. 8.** Amount of CO adsorption over Pt-$SO_4$/$ZrO_2$(S) after reduction (●) and reaction (▲) and Pt-$SO_4$/$ZrO_2$(A) after reduction (■); Pt-$ZrO_2$ after reaction (□).

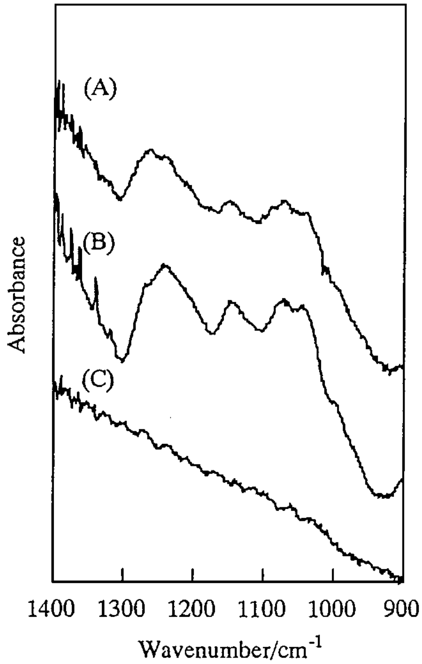

**FIG. 9.** IR spectra of 3% Pt-$SO_4$/$ZrO_2$(S) after calcination (A), after reduction (B), and after reaction (C).

addition, although it was in proportion to the catalytic activity for the coupling of methane. It is indicative of the growing aggregation of the metal during reaction, but in comparison with the samples before reaction an increase of the peak strength of Pt in the XRD curve is not observed. Pretreatment with $H_2$ at 500°C was done before the measurement was carried out to remove the carbon materials after reaction.

Platinum-doped $ZrO_2$ without sulfation showed the chemisorbed value close to that of the sample sulfated with sulfuric acid (Fig. 8). Since the sample is active for the coupling (0.2% in conversion), it is assumed that the value is equivalent to the number of active surface atoms of Pt. Thus, based on an adsorption stoichiometry of unity of CO-chemisorbed/Pt-surface atom, calculation of the CO value of 3% Pt-$SO_4$/$ZrO_2$(S), highest in activity, leads to the ratio of CO/Pt = 0.09, where 9 atoms per 100 adsorb CO and convert methane into $C_2$ species. The turnover frequencies (TOF) for the reaction are also estimated from the conversion of 0.23% to be 0.18 min$^{-1}$, those for other catalysts being 0.13–0.16 min$^{-1}$ as shown in Table 1.

Experiments using an IR instrument were carried out in order to elucidate the relation between the sulfate species and Pt; the spectra of 3% Pt-$SO_4$/$ZrO_2$(S) are shown in Fig. 9. The superacid of $SO_4$/$ZrO_2$ shows characteristic adsorption bands at 980–1230 cm$^{-1}$, which are assigned to the bidentate sulfate coordinated to metal elements (10–12). The adsorptions at 1050, 1140, and 1240 cm$^{-1}$, which are analogous to those bands, are observed with the samples after calcination and reduction, but the adsorption peaks vanish after reaction. The catalyst was deeply colored after reaction, and the sulfate materials were removed by reduction during the induction period as shown in Fig. 1, although the reduction did not occur while pretreating with $H_2$ at the same temperature as the coupling reaction. It is noteworthy that the catalyst cannot be reduced to desulfurize the surface in flowing hydrogen in the presence of Pt at 500°C.

Since investigation of the relation between sulfate and Pt at the steady state of reaction was found difficult using the ir analysis, experiments using TG-DTA were performed. The TGA in air of the sulfated zirconia matter shows a weight decrease at 640–1000°C, which is caused by the decomposition of sulfate on the surface to form $SO_2$ (18–20). The weight decrease leads to the sulfur content, whose values agree well with those of the elemental analysis. Quantities of the loaded sulfur estimated from a weight loss at 600–1000°C are shown in Table 2, a large decrease being seen

**TABLE 2**

**Thermal Gravimetrical Analysis of Sulfur in the Pt-$SO_4$/$ZrO_2$(S) Catalysts**

| Quantity of Pt (%) | Quantity of S (wt%) | |
|---|---|---|
| | Before reduction | After reaction |
| 0 | 3.2 | 0.4 |
| 1 | 2.0 | 0.5 |
| 3 | 2.2 | 0.6 |
| 5 | 3.2 | 0.8 |
| 7.5 | 2.5 | 1.5 |

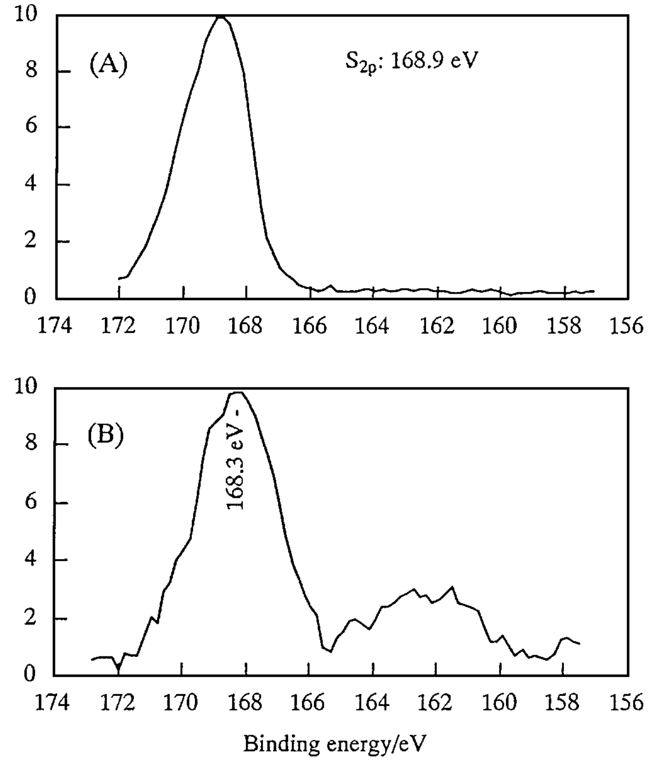

**FIG. 10.** XPS spectra of S(2p) for 3% Pt-$SO_4/ZrO_2$(S) after calcination (A) and after reaction (B).

for the samples after reaction. The values determined can lead to the calculation of a Pt number per the surface S atom. The ratios of Pt/S were 0.4, 0.9, 1.0, and 0.8 mol/mol for 1, 3, 5, and 7.5% Pt-$SO_4/ZrO_2$(S) after reaction, respectively; the values before reduction were 0.1, 0.2, and 0.4 for 1, 3, and 7.5% Pt-sample, respectively. Thus, it is concluded that the ratio of Pt to S on the active catalysts of 3–7.5% Pt-$SO_4/ZrO_2$(S) is unity during reaction, the S amount per Pt being more than 2.5 before reaction.

Measurements of XPS were carried out in order to characterize S and Pt, the spectra of S and Pt of 3% Pt-$SO_4/ZO_2$(S) being shown in Figs. 10 and 11, respectively. The binding energy of S (2p) after reaction was 168.3 eV, quite similar to that before reduction, 168.9 eV, whose value agreed with that of metal sulfates (10,11). The state of S is $SO_4^{2-}$. A new peak at 162 eV after reaction shows the state of $S^{2-}$ (21), indicating the reduction of part of the $SO_4^{2-}$ during the reaction.

The binding energy of Pt (4f) is known to be 71.7, 72.6, and 74.5 eV for $Pt^0$, $Pt^{+2}$, $Pt^{+4}$, respectively (22,23). The spectra showed the platinate to be reduced from calcination (A), through reduction (B), to reaction (C). The binding energy of 71.4 eV after reaction showed platinum to be in the metallic state, and the peak area was estimated to be around 10%, which was close to the chemisorbed value of CO.

In consideration of the results, it is proposed that an active site (in the steady state) is created by interaction of a Pt metal with a sulfated zirconia, Pt-$SO_4$-$ZrO_2$, which is obtained by sulfation of the zirconia gel with sulfuric acid, followed by the addition of platinum. This species is surrounded by 10 times platinate-$SO_4/ZrO_2$ with various oxidation numbers of Pt, except 0, when 3 wt% Pt is added and protected from aggregation. Platinums without the sulfate or with the matter sulfated with ammonium sulfate gather together during reaction to result in deactivation. As for superacidity, the sulfate-metal oxides obtained by the treatment with sulfuric acid are usually higher in activity, as well as acidity, than those with ammonium sulfate (10,11). The latter substances are gradually decomposed during reaction at the present high temperature because of weak interaction of the sulfate species with the $ZrO_2$ support, resulting in the condensation of Pt. The fact that the sulfation with

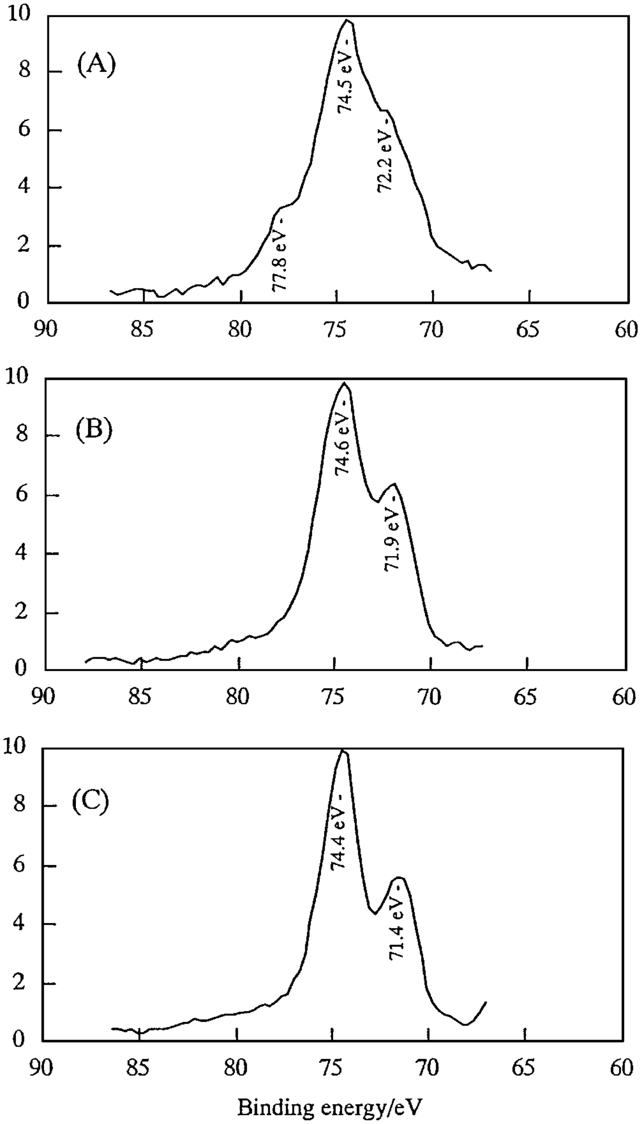

**FIG. 11.** XPS spectra of Pt(4f) for 3% Pt-$SO_4/ZrO_2$(S) after calcination (A), after reduction (B), and after reaction (C).

sulfuric acid gives the higher dispersion of Pt also supports its superiority as a catalyst.

## REFERENCES

1. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 903 (1986).
2. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Am. Chem. Soc.* **107**, 5062 (1985).
3. Campbell, K. D., and Lunsford, J. H., *J. Phys. Chem.* **92**, 5792 (1988).
4. Nelson, P. F., Lukey, C. A., and Cant, N. W., *J. Phys. Chem.* **92**, 6176 (1988).
5. Murata, K., Hayakawa, T., and Fujita, K., *J. Chem. Soc. Chem. Commun.*, 221 (1997).
6. Miao, Q., Xiong, G. X., Li, X. S., Sheng, S. S., and Guo, X. X., *Catal. Lett.* **41**, 165 (1996).
7. Pitchai, R., and Klier, K., *Catal. Rev.-Sci. Eng.* **28**, 13 (1986).
8. Lunsford, J. H., *Angew. Chem. Int. Ed.* **34**, 970 (1995).
9. Voskresenskaya, E. N., Roguleva, V. G., and Anshits, A. G., *Catal. Rev.-Sci. Eng.* **37**, 101 (1995).
10. Arata, K., *Adv. Catal.* **37**, 165 (1990).
11. Arata, K., and Hino, M., *Mater. Chem. Phys.* **26**, 213 (1990).
12. Arata, K., *Appl. Catal. A: General* **146**, 3 (1996).
13. Hino, M., and Arata, K., *Catal. Lett.* **30**, 25 (1995).
14. Hino, M., and Arata, K., *J. Chem. Soc. Chem. Commun.*, 789 (1995).
15. Hino, M., and Arata, K., *Catal. Lett.* **34**, 125 (1996).
16. Matsuhashi, H., Sakurai, K., and Arata, K., *Chem. Lett.*, 585 (1989).
17. Matsuhashi, H., Hisazaki, T., and Arata, K., *in* “Proc. 9th Soviet–Japanese Seminar on Catal., Yuzhno-Sakhalinsk, 1990,” p. 33.
18. Hino, M., Kobayashi, S., and Arata, K., *J. Am. Chem. Soc.* **101**, 6439 (1979).
19. Srinivasan, R., Keogh, R. A., and Davis, B. H., *Appl. Catal. A: General* **130**, 135 (1995).
20. Arata, K., *Petrotech* **19**, 733 (1996).
21. Jin, T., Machida, M., Yamaguchi, T., and Tanabe, K., *Inorg. Chem.* **23**, 4396 (1984).
22. Sayari, A., and Dicko, A., *J. Catal.* **145**, 561 (1994).
23. Wagner, C. D., NIST XPS DATABASE (1989).