Platinum-added Sulfated-zirconia Effective for Highly Selective Dehydrogenative Coupling of Methane

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(Received December 1, 1997; CL-970903)

An active and stable catalyst of 3 wt% Pt-added sulfated-zirconia for the dehydrogenative coupling of methane is obtained by impregnating zirconia gel with 0.5 mol dm^{-3} 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; this catalyst gave 40% conversion of the equilibrium value with 100% selectivity at 500 °C.

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. A number of catalytic systems that show methane conversions and C_2 hydrocarbon selectivities have been reported, several reviews being also found.[1-3] However, many kinds of catalyst systems still need high temperatures to get the satisfactory activity and selectivity, 700 °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 developed.

We have demonstrated that impregnation of the sulfated-zirconia (SO_4/ZrO_2) with noble metals such as Pt and Pd leads to pronounced activity for the reaction of butane to isobutane, the Pt concentration being 7-8 wt%; the catalyst with Pt was highest in activity for the reaction, more active than any solid catalyst reported.[4-5] 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 over Pt-SO_4/ZrO_2 without using O_2 as the oxidant.

First zirconia gel was obtained by hydrolyzing $ZrOCl_2$ with aqueous ammonia to pH 8 at temperature of 50-60 °C; aqueous ammonia solution (25%, ~15 cm^3) was added dropwise with stirring into 25 g of $ZrOCl_2{\cdot}8H_2O$ dissolved in 500 cm^3 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 cm^3 of hot water for each, and drying at 110 °C.

Two grams of the gel (20-30 mesh) were immersed in 30 cm^3 of 0.5 mol dm^{-3} 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 cm^3 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 residual water, drying, and finally calcining in air at 600 °C for 3 h.

The coupling reaction was carried out at atmospheric pressure in a single-pass fixed-bed reactor with 0.5 g of catalyst (20-30 mesh). The reduction of catalyst was performed in hydrogen at a flow rate of 10 cm^3/min at 500 °C for 1 h before reaction. After the pretreatment methane was introduced at a rate of 10 cm^3/min without any carrier gas, and effluent products were analyzed with an on-line gas chromatograph (Porapack R-2 m, 30 °C).

The dehydrogenative reaction without any oxidant was carried out over the Pt-SO_4/ZrO_2 catalysts. With 3 wt% Pt a steady conversion of 0.2% was observed between 100 and 180 min at 500 °C after a rapid increase of conversion in the first 20 min as shown in Figure 1, 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. 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 catalytic activity dropped, while the conversion recovered its normal steady state activity when hydrogen was released. 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.

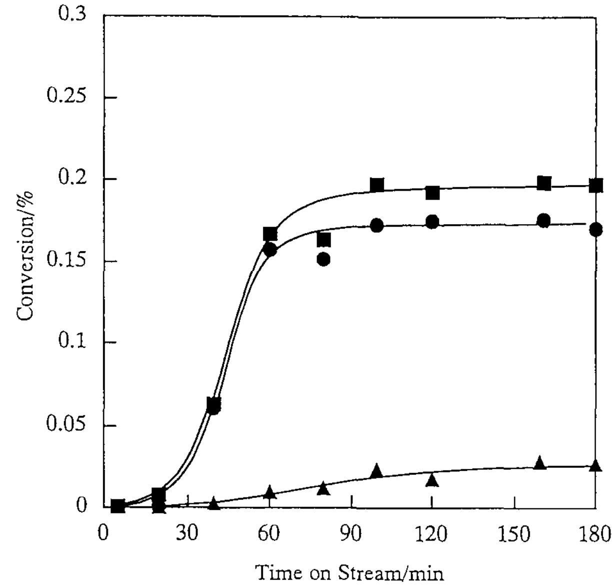

Figure 1. Reaction of methane over 3 wt% Pt-SO_4/ZrO_2 at 500°C. (■) Conversion, (●) Ethane, (▲) Ethylene.

Table 1 summarizes the highest activities and the selectivities

Table 1. Activities of Pt-SO_4/ZrO_2 with various amount of Pt for reaction of methane at 500°C

Quantity of Pt /wt%	Conversion /%	Selectivity /%		
		C_2H_6	C_2H_4	CO_2
0	0.08	0	0	100
1	0.12	88	12	0
3	0.23	90	10	0
5	0.23	91	9	0
7.5	0.19	90	10	0

in several runs over the Pt-SO_4/ZrO_2 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. 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 methane reacted, and the deposition was not concerned with the catalytic activity.

It is indicative that the active site for the coupling is metallic platinum. Thus, Pt-loaded zirconia without the sulfation (Pt-ZrO_2) was prepared in the same manner as the Pt-SO_4/ZrO_2 matter. The 3% Pt-ZrO_2 catalyst showed the highest conversion of 0.20% at 60 min, but large decrease of the conversion, afterward, was observed.

As far as the XRD analysis was concerned, it was shown that impregnating zirconia gel with sulfuric acid led to quite high dispersion of the Pt matter onto the support, even though relatively large amounts of platinate were added.[5]

The dispersion, or fraction of surface Pt atoms, was measured volumetrically by CO chemisorption at room temperature using a pulse reactor with a fixed-bed catalyst, equipped with calibrated bulbs. The amount of CO adsorption on the catalysts after reaction stayed constant (12-13 μ mol/g) from 3 to 7.5% of the Pt addition, being in agreement with the catalytic activity for the coupling of methane.

Three percent Pt-ZrO_2 without sulfation showed the amount of chemisorbed CO of 13 μ mol/g, quite close to that of the sulfated sample with 3% of Pt. 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 atom of Pt. 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, highest in activity, led to the ratio of CO/Pt = 0.09, where 9 atomes per 100 ones adsorbed CO and converted methane into C_2 species.

Quantities of the loaded sulfur were estimated from a weight loss at 640-1000 °C, caused by the decomposition of sulfate on the surface, using TG-DTA. The values were 0.5, 0.6, 0.8, and 1.5 S wt% for 1, 3, 5, and 7.5% Pt-SO_4/ZrO_2 after reaction, respectively. The determined values can be led 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, 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 is unity during reaction.

Measurements of XPS were carried out in order to characterize S and Pt. The binding energy of S 2p after reaction was 168.3 eV, whose value agreed with that of SO_4^{2-}.[6,7] The spectra of Pt of 3% Pt-SO_4/ZrO_2 are shown in Figure 2. The binding energy of Pt 4f is known to be 71.7, 72.6, and 74.5 eV for Pt^0, Pt^{+2}, and Pt^{+4}, respectively.[8,9] 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 the 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 zirconia gel with sulfuric acid followed by addition of platinum. This species is surrounded by ten 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 gather together during reaction to result in deactivation.

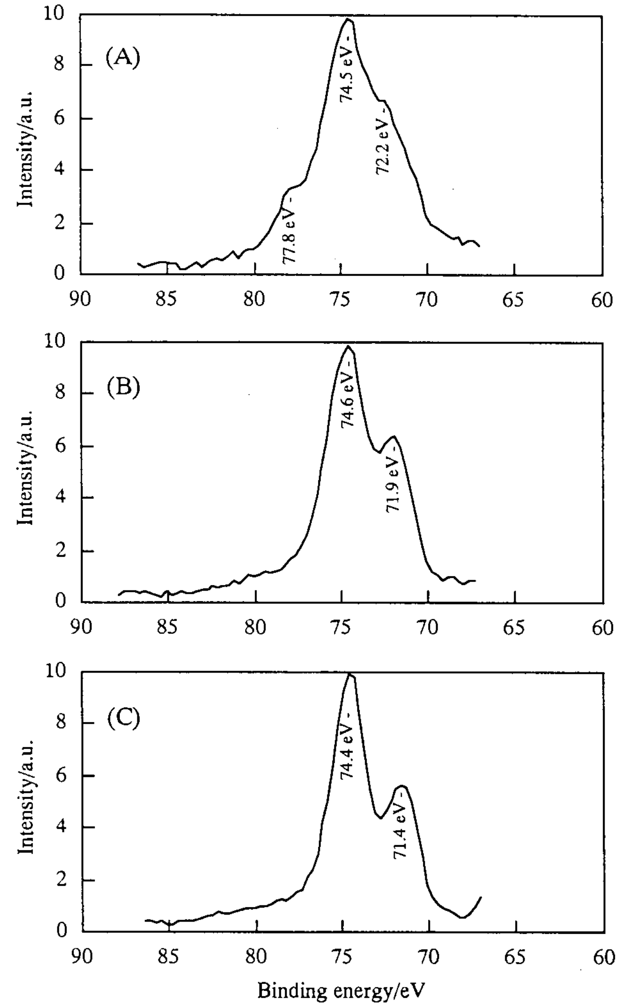

Figure 2. XPS spectra of Pt 4f for 3 wt% Pt-SO_4/ZrO_2 after calcination (A), after reduction (B), and after reaction (C).

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