Photo-Oxidative Coupling of Methane over TiO_2-based Catalysts

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Oxidative coupling of methane was carried out under UV-irradiation at temperatures below 500 K. C_{2+} hydrocarbons were formed over TiO_2 catalysts prepared from $Ti(i\text{-}OPr)_4$ by hydrolysis. Correlation between C_{2+} selectivity and anatase fraction (%-anatase) of the catalysts was observed.

Although many efforts have been made for oxidative coupling of methane (OCM) at low temperatures,[1] only a few are reported to obtain meaningful C_{2+} hydrocarbons at a temperature below 573 K. It is reported that some oxygenates (HCHO and CH_3OH) were formed from CH_4 and O_2 over high-dispersed MoO_3- and V_2O_5-based catalysts with UV-irradiation at temperatures below 550 K.[2] The C_{2+} hydrocarbon selectivity was, however, negligible. Kuzmin *et al.* reported C_{2+} hydrocarbon formation by TPD from photo-adsorbed CH_4 over TiO_2.[3] However, the process was not catalytic. Gratzel *et al.* reported deep oxidation of CH_4 to CO and CO_2 over $(SiW_{12}O_{40})^{4-}/TiO_2$ by photo-excitation,[4] but they did not obtain C_{2+} hydrocarbons. In the present paper, it is reported for the first time to obtain C_{2+} selectivity of ca. 4% with CH_4 conversion of 13% at 473 K under UV-irradiation over home-made TiO_2 catalysts.

A closed circulation system (V = 376 cm^3) was used for the reaction. A specially designed multi-layered reaction vessel made of quartz glass is illustrated in Figure 1. For high efficiency of UV-irradiation, a high pressure mercury lamp (100 W) was installed at the center of the vessel. By evacuating between the cooling jacket and the reactor, UV-irradiation could be applied at higher temperatures than 300 K. Catalyst powder (5.0 g) were suspended in 10 cm^3 of distilled water. The internal wall of the reactor was coated with the catalyst slurry (shown as x in Figure 1), and dried *in vacuo* at 373 K for 1 h. Pre-mixed reaction gas (40 kPa) was introduced into the reactor, and heated up to a temperature T = 373-473 K. UV-irradiation was applied at reaction temperature, which was monitored by a thermocouple in contact with the external wall of the reactor. The reaction gas was well-mixed by a circulation pump, and a part of the gas was sampled periodically to analyze the products by gas chromatography.

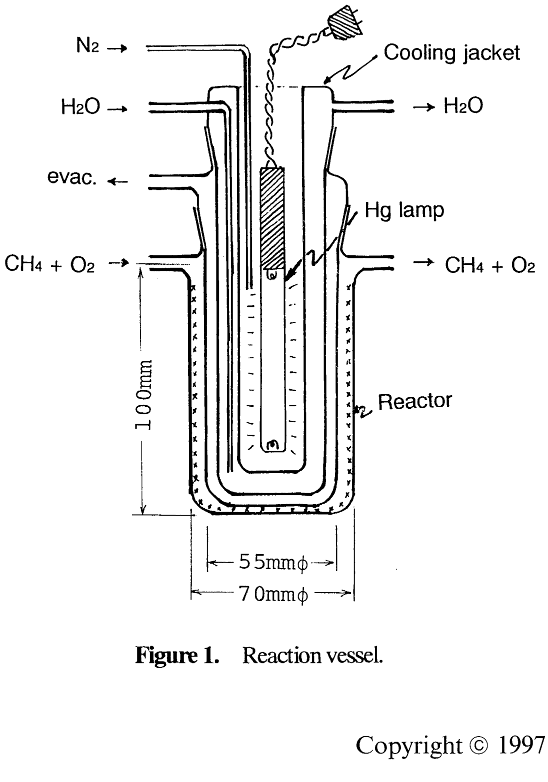

Figure 1. Reaction vessel.

Table 1. Characteristic properties of TiO_2 catalysts

Catalyst No.	Precursor	T_c[a] / K	Crystal form	BET[b] / m^2g^{-1}	L[c] / nm	λ[d] / nm
#1	$TiCl_4$	473	rutile	74.3	12-20	412
#2	$TiCl_4$	773	rutile	48.1	15-23	412
#3	$TiCl_4$	973	rutile	34.5	20-29	413
#4	$Ti(i\text{-}PrO)_4$	473	anatase	87.0	12	379
#5	$Ti(i\text{-}PrO)_4$	573	anatase	38.0	13	382
#6	$Ti(i\text{-}PrO)_4$	773	anatase	19.7	20	395
#7	$Ti(i\text{-}PrO)_4$	873	anatase	3.9	40	
			+ rutile (70%)		82	418

[a] Calcination temperature. [b] BET Surface area. [c] Crystallite size. [d] UV- absorption edge.

Titanium oxide catalysts were prepared by hydrolysis of $TiCl_4$ or $Ti(i\text{-}OPr)_4$ solutions, washed with distilled water thoroughly, and then calcined at a temperature between 473 and 973 K for 5 h. The crystallite size was evaluated by XRD peak broadening, as listed in Table 1. The anatase content (%-anatase) of TiO_2 was estimated by XRD peak intensities, according to the equation reported by Spurr *et al.*[5] The TiO_2 catalysts (#1-3) prepared from $TiCl_4$ were in rutile form with morphological anisotropy, which was elucidated by the broadening of XRD peaks and the SEM images. The residual Cl was not detected by XPS. The UV absorption edge was ca. 412 nm, corresponding to a smaller band gap than anatase by 0.2 eV. The TiO_2 catalysts prepared from $Ti(i\text{-}OPr)_4$ and calcined at 473-773 K (#4-6) were in anatase form. The crystallinity increased and sintering occurred by calcination. The UV spectra showed blue-shift of the absorption edge (λ) when the anatase crystallite was small. By calcination at 873 K, the crystal was partially transformed into rutile (#7). The anatase content of the catalyst #7 was estimated at ca. 30%. Commercial TiO_2 (P-25) purchased from Nippon Aerosil Co., Ltd. was used as a reference catalyst. The anatase content of P-25 was estimated at ca. 70%. X-Ray

Table 2. Photo-oxidative coupling of methane over TiO_2 catalysts [a]

Run	Catal.	T / K	CH_4/O_2	CH_4	Selectivity / C - %				
No.	No.		ratio [b]	conv./%	CO_2	CO	C_2H_6	C_3H_8	C_{2+}
blank 1 [c]	#6	473	4	0.0	-	-	-	-	-
blank 2 [d]	#6	473	-	0.1	-	-	-	-	-
1	#1	473	4	11.3	99.4	0.3	0.3	-	0.3
2	#2	473	4	11.9	97.9	1.9	0.1	-	0.1
3	#3	473	4	11.6	98.6	1.4	-	-	-
4	#4	473	2.5	20.4	95.8	3.2	0.9	0.0	1.0
5	#4	473	4	12.6	93.9	4.3	1.8	0.0	1.8
6	#4	473	9	7.6	91.3	6.0	2.6	0.1	2.7
7	#5	473	4	12.6	94.6	3.2	2.2	0.0	2.2
8	#6	373	4	13.7	94.7	1.5	3.6	0.2	3.8
9	#6	423	4	12.5	94.3	1.9	3.8	0.1	3.9
10	#6	473	4	13.0	93.0	3.0	3.9	0.1	4.0
11	#7	473	4	12.0	98.8	0.8	0.4	-	0.4
12	P-25	473	4	12.5	97.3	1.3	1.4	0.0	1.4

[a] Reaction results at t = 20 h.
[b] Initial ratio ($P^0 = 40$ kPa).
[c] Without UV-irradiation.
[d] Feed gas : CH_4 alone.

photoelectron spectra of used catalysts showed that the surface TiO_2 was not reduced at all even after 4 runs of the reaction.

The time course of OCM reaction with UV-irradiation showed that CO and CO_2 were produced with O_2 consumption in the early stage of reaction, followed by the formation of C_{2+} hydrocarbons. Since the product selectivity converged within 20 h of the reaction, the catalytic properties hereafter were evaluated by the selectivity at this time (t = 20 h). The reaction results at 373-473 K for 20 h were summarized in Table 2. Blank tests were carried out over anatase catalysts. No products were detected without UV-irradiation (blank 1). Any products were negligible, when CH_4 alone was used as the reaction gas (blank 2). Deep oxidation to CO_2 was predominant over rutile catalyst (#1-3) irrespective of the calcination temperature, when initial $CH_4 / O_2 = 4$ (run 1-3). In contrast, C_{2+} hydrocarbons were formed with C-based selectivity of 1.8-4.0% by OCM reaction with UV-irradiation over anatase catalysts (#4-6) at standard reaction conditions (T = 473 K, initial $CH_4 / O_2 = 4$), and most of the hydrocarbons were paraffin. The selectivity was inclined to increase with the crystallinity evaluated by crystallite size (run 5, 7, and 10), suggesting that well-crystallized anatase was preferable to suppress deep oxidation. The formation of C_{2+} hydrocarbons at a temperature below 500 K is unprecedented, by considering the results of the conventional OCM reaction over TiO_2 catalysts that the deep oxidation to CO_x is predominant at a high temperature while the catalysts are almost inactive at a low temperature. A commercial TiO_2 catalyst P-25 and the catalyst #7 (the mixture of anatase and rutile) showed moderate C_{2+} selectivity (run 11, 12). Correlation between %-anatase and C_{2+} selectivity was observed, suggesting that the active component of the catalysts for C_{2+} hydrocarbons may be in anatase form.

Table 2 also shows the effect of reaction conditions on product selectivity. The selectivity to CO and C_{2+} hydrocarbons increased and CO_2 selectivity decreased with the initial CH_4 / O_2 ratio of reaction gas (run 4-6). The selectivities to CO and C_{2+} hydrocarbons slightly increased with temperature (run 8-10). The desorption of these products from catalyst surface may be promoted at higher temperature. The precise photo-activation process of methane is now under investigation, and will be reported later.

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