Photoinduced non-oxidative coupling of methane over silica-alumina and alumina around room temperature

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Received (in Cambridge, UK) 2nd September 1998, Accepted 18th September 1998

Around room temperature, photoinduced coupling of methane proceeds without any oxidant molecules on silica-alumina and alumina evacuated at 1073 K; many coupling products in the gaseous phase are obtained from silica-alumina, while most of products on alumina are obtained only through thermal desorption.

The oxidative coupling of methane is an expedient reaction to convert natural gas into useful chemicals. However, it is very difficult to obtain the coupling products in high yield, because oxidation of the coupling products to CO_x proceeds more selectively than the coupling reaction. If the oxidant molecules are removed to avoid complete oxidation, the reaction requires very high temperature[1] and has no practical use. Photoinduced reactions are one of the most available reactions taking place at low temperature where complete oxidation could be minimized. Recently, it was reported that photo-induced coupling of methane proceeded at 373–473 K in the presence of oxygen over TiO_2[2] which is the most widely used photocatalyst. However the selectivity of CO_x was very high and the yield of coupling products was only *ca.* 0.5%. Use of N_2O as oxidant improved the selectivity of coupling products on MgO, but the yield was $< 0.2\%$.[3,4] The possibility of the photoinduced non-oxidative coupling, where no oxidant molecules are employed, was suggested by using transition metal oxides, such as V/SiO_2,[5] TiO_2[6] and Mo/SiO_2.[7] However, the highest yield was only *ca.* 0.007% in the gaseous phase and $< 0.4\%$ even after forced desorption by heating or by admission of water vapor.[7]

Here, we describe that the coupling products are obtained in yields as high as 5% without formation of CO and CO_2 in the non-oxidative coupling of methane over silica-alumina and alumina under photoirradiation. Silica-alumina, which is a member of silica-based materials recently attracting a great deal of attention as a new photocatalyst family,[8–13] was found to be photoactive; it exhibited a characteristic phosphorescence emission spectrum.[9] The photoreactivity of silica-alumina toward gaseous molecules, however, has not been investigated, and the present report is the first in this area.

The silica sample was prepared from $Si(OEt)_4$ by the sol–gel method followed by calcination in dry air at 773 K[14] and its specific surface area was 679 $m^2\ g^{-1}$. The silica-alumina samples, SiO_2–Al_2O_3(L) and SiO_2–Al_2O_3(H), employed were reference catalysts of the Catalysis Society of Japan, JRC-SAL-2 and JRC-SAH-1, respectively.[15,16] The alumina contents were 13.75 and 28.61 mass% and the specific surface areas were 560 and 511 $m^2\ g^{-1}$, respectively.[15,16] The alumina sample was also the JRC sample, JRC-ALO-4 (surface area; 174 $m^2\ g^{-1}$).[15,16]

The reaction tests were carried out in a closed quartz reaction vessel (82 cm^3). The sample (1.0 g) was spread on the flat bottom of vessel (19.6 cm^2), and was treated with 60 Torr (1 Torr = 133 Pa) O_2 for 1 h at 1073 K, followed by evacuation for 1 h at 1073 K. Methane (99.95%) was purified by a vacuum evaporation before use and introduced into the reactor. The initial pressure of methane (100 μmol) in the reactor was 21 Torr and no oxidant molecules were introduced. The sample was irradiated with a 250 W Xe lamp for 18 h. Under photoirradiation, the temperature of the sample bed was measured to be *ca.* 310 K. Products in the gaseous phase were collected with a liquid-N_2 trap and analysed by GC. Then adsorbed products were thermally desorbed by heating (573 K, 15 min), collected, and analysed by GC.

Table 1 shows the product yields in photoinduced non-oxidative coupling of methane, in the absence of gaseous oxidants, over silica, silica-alumina and alumina. Note that in all cases no oxygenates (MeOH, HCHO, CO_2, CO) were detected.

For the empty reactor (run 1), only a trace amount of C_2H_6 was formed upon photoirradiation. On the silica sample (run 2), a small amount of C_2H_6 and C_3H_8 were obtained in the gaseous phase, and a trace amount of C_2H_4 and C_3H_6 were observed as the thermally desorbed products.

Over the silica-alumina samples (runs 3 and 4), the conversions were obviously much higher than that over silica. In the gaseous phase, a large amount of C_2–C_4 alkanes was obtained while smaller amounts of C_2–C_6 alkanes and alkenes were desorbed upon heating. Among the thermally desorbed products, alkenes were the major products. In the dark (in an electric furnace, run 6) at 473 K, no products were detected, clearly indicating that photoirradiation is necessary for the above reaction. On SiO_2–Al_2O_3(L), the total yield reached

Table 1 Results of photoinduced non-oxidative coupling of methane[a]

		Yield of gaseous phase product (C%)[b]				Yield of thermal desorption product at 573 K (C%)[b]								Total
Run	Sample	C_2H_6	C_3H_8	C_4H_{10}	Total	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C5,6	Total	(C%)[b]
1[c]	—	tr.	0	0	tr.	—	—	—	—	—	—	—	—	tr.
2	SiO_2	0.08	0.01	0	0.09	tr.	0	tr.	0	0	0	0	tr.	0.09
3	SiO_2–Al_2O_3(L)	3.54	0.85	0.14	4.53	0.42	0.01	0.27	0.02	0.20	tr.	0.45	1.37	5.90
4	SiO_2–Al_2O_3(H)	1.82	0.27	0.03	2.12	0.29	0.02	0.24	0.01	0.12	tr.	0.22	0.90	3.02
5	Al_2O_3	0.48	0.02	0	0.50	0.33	2.64	0.03	1.18	0	0.49	0.16	4.83	5.33
6[d]	SiO_2–Al_2O_3(L)	0	0	0	0	0	0	0	0	0	0	0	0	0
7[d]	Al_2O_3	0	0	0	0	0	0	0	0	0	0	0	0	0

[a] Reaction temperature = *ca.* 310 K, reaction time = 18 h, CH_4 = 100 μmol. [b] Based on the initial amount of CH_4. [c] A blank test. [d] Reaction at 473 K without UV-irradiation. tr. = trace.

5.90% and the yield of gaseous phase products reached 4.53%, much higher than those in any other reports on photoinduced coupling of methane.[2–7] It should be noted that no oxidant molecules were introduced in the reaction system and that the temperature of the sample bed, measured by a thermocouple, was only 310 K. The total yield on SiO_2–Al_2O_3(L) was higher than that on SiO_2–Al_2O_3(H). It is reported that SiO_2–Al_2O_3(L) has a larger phosphorescent emission spectrum with fine structure and a clearer peak in its excitation spectrum than SiO_2–Al_2O_3(H). From this result, it is proposed that highly dispersed aluminum species in the silica tetrahedral matrix are responsible for the photoactivity of silica-alumina. In the present case, such species would also play an important role in the photoinduced reaction.

On the alumina sample (run 5), the total yield (5.33%) was as high as that on the silica-alumina sample [SiO_2–Al_2O_3(L)]. Alumina exhibited no activity in the dark (run 7), indicating that photoirradiation is also necessary for the reaction over alumina. However, the feature of reaction on alumina was different from that on silica-alumina; on alumina, the yields of gaseous phase products (C_2H_6 and C_3H_8) were much lower and the most of products were obtained on heating. Among the thermal desorption products, alkanes were dominant on alumina, while they were minor products on silica-alumina.

In conclusion, it was found that the coupling of methane proceeded under photoirradiation on silica-alumina and alumina in the absence of any oxidant molecules. A meaningful amount of coupling products was obtained without the formation of CO and CO_2. Specially, silica-alumina, whose alumina content is lower, exhibited the highest activity without any thermal desorption.

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Communication 8/06825I