Photoactivation of Methane on Metal Ion-Supported Silica Gel

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(Received August 28, 1995)

Photoactivation of methane has been investigated on metal ion-supported silica gels. Methyl radicals were detected on Na, Mg, Ca, Sr, Y, Ti, Zn, Zr, Sn, Pb and Bi/SiO_2 at 77 K by electron spin resonance (ESR). It is found that methane was dissociated to the methyl radical on Na, Mg, Sr, Zn and Sn supported samples with lower photon energy than C-H bond dissociation energy in methane.

Materials for the dissociation of C-H bonds in methane and stabilization of the resulting free radicals are desired for the selective conversion of methane, since the methyl radical may be an intermediate in the oxidative coupling reaction[1] and partial oxidation[2] of methane. Methane decomposes to methyl radicals on B, V and Mo supported on silica gels and Porous Vycor Glass (PVG) under UV irradiation even at 77 K.[2,3,4] Using Al supported on silica gel, we obtained a polymerized radical directly from methane under UV light irradiation at 77 K.[5] In this study, the photoactivation of methane on various metal ions-supported silica gels was investigated using ESR at 77K.

Metal ions-supported silica gels were prepared by impregnating silica gel (Davison 950) with the corresponding metal salt solutions, followed by drying at 50 °C in a rotary evaporator and calcination in air at 600 °C. The samples contained 0.5-1 wt% dopants. Prior to UV irradiation, each sample was oxidized at 500 °C under oxygen to remove the surface organic impurities. UV light irradiation was carried out using a super-high-pressure mercury lamp (Ushio Electric Co., Ltd., USH-500D) equipped with an infrared cut-off filter, 40 cm away from the sample. To determine the effective wave length of UV light for photoactivation, the samples were exposed to filtered UV light using sharp cut filters (Kenko Co., Ltd.) of $250 \leq \lambda \leq 390$ nm, $\lambda \geq 280$ nm, $\lambda \geq 300$ nm and $320 \leq \lambda \leq 380$ nm. Methane (Takachiho Kagaku Cogyo K.K., 99.99%) and deuteromethane (Cambridge Isotope Laboratories, 99% D) were used without further purification.

Figure 1(a) shows the ESR spectrum for 1 wt% Mg/SiO_2 with UV irradiation under methane atmosphere at 77 K. The signal indicates a hyperfine structure of four lines with hyperfine splitting of 19.0 G and an intensity ratio of 0.2: 3.0: 5.4: 0.4. When the same experiment was carried out on the catalyst under deuteromethane atmosphere, a seven-line signal with hyperfine splitting of 3.0 G and an intensity ratio of 0.6: 1.8: 5.0: 7.0: 6.1: 3.2: 0.7 was observed (Figure 1(b)). Based on the nuclear spin of the proton (I_H=1/2) and deuteron (I_D=1), the signals were assigned to the methyl radical, although ESR parameters differed from those of normal planar methyl and deuteromethyl radicals having hyperfine splitting of 23 and 3.5 G with line intensity ratios of 1: 3: 3: 1 and 1: 3: 6: 7: 6: 3: 1, respectively. Smaller hyperfine splittings of 21.2-19.3 G were preferentially reported for methyl radicals on solid surfaces at 77 K.[4,6,7] The radicals on the examined catalysts have a non-planar structure, probably square pyramidal, due to a strong interaction with the solid[6], as

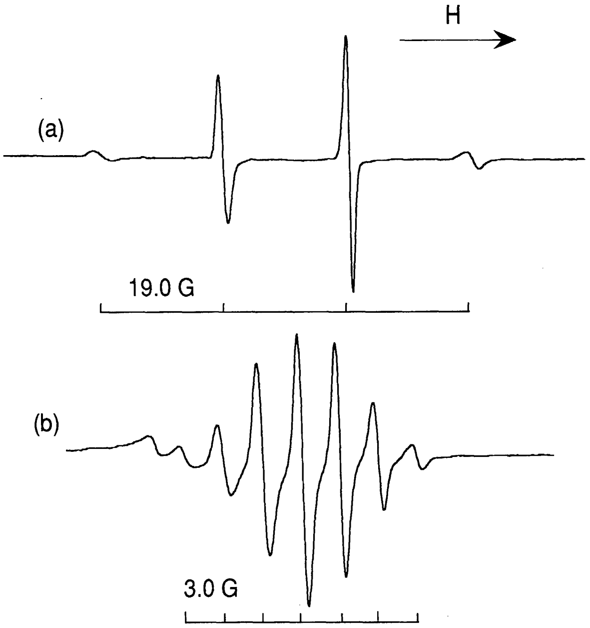

Figure 1. ESR spectra obtained on Mg/SiO_2 under UV irradiation in 50 torr of (a)CH_4 and (b)CD_4 at 77 K.

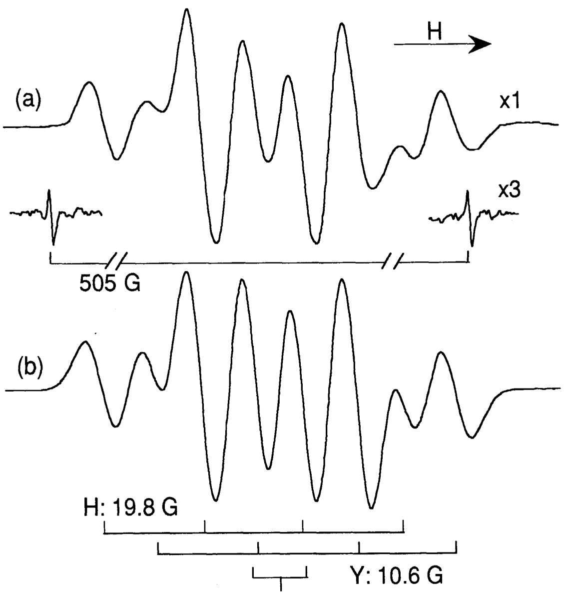

Figure 2. (a)ESR spectrum obtained on Y/SiO_2 under UV irradiation in 50 torr of CH_4 at 77 K; (b)simulation calculated with the ESR parameters of A_H=19.8 G, A_Y=10.6 G and Lorentzian line width of 3.8 G.

Table 1. Hyperfine splitting of the methyl radical and effective wave length for the activation of methane over metal ion-supported silica gels

Catalysts	Hyperfine Splitting/ G	Wave length of irradiation light/nm[a]			
		$\lambda \geq 250$	$\lambda \geq 280$	$\lambda \geq 300$	$\lambda \geq 320$
1wt% Ca/SiO_2	20.6	+	-	-	-
1wt% Y/SiO_2	19.8	+	-	-	-
1wt% Ti/SiO_2	18.5	+	-	-	-
1wt% Zr/SiO_2	18.6	+	-	-	-
1wt% Bi/SiO_2	23.0	+	-	-	-
1wt% Sr/SiO_2	20.6	+	+	-	-
0.5wt%Na/SiO_2	19.3	+	+	+	-
1wt% Mg/SiO_2	19.0	+	+	+	+
1wt% V/SiO_2	22.9	+	+	+	+
1wt% Mo/SiO_2	22.8	+	+	+	+
1wt% Zn/SiO_2	17.2	+	+	+	+
1wt% B/SiO_2	19.8	+	+	+	+
1wt% Sn/SiO_2	16.7	+	+	+	+
1wt% Pb/SiO_2	23.0				
CH_3I on SiO_2	22.7[b]				

[a] "+" and "-" indicate the effective and non-effective for activation, respectively. [b] This methyl radical was derived from methyl iodide on a silica gel surface.

reported by Kubota and co-workers.

Figure 2(a) shows the ESR spectrum for 1 wt% Y/SiO_2 with UV irradiation under methane atmosphere. The signals each have a set of eight lines and a set of two lines, the latter being assigned to the hydrogen radical with hyperfine splitting of ca. 505 G. The former signal is possibly a methyl radical split by the nuclear spin of yttrium ($I_Y=1/2$). Since a simulation calculated by the program, POW,[8] with ESR parameters of hyperfine splitting of 19.8 G (hydrogen), 10.6 G (yttrium) and Lorentzian line width of 3.8 G, shown in Figure 2(b), well reproduces the observed signal, the radical seems to interact with yttrium strongly.

Furthermore, the photoactivation of methane was carried out on silica gel catalysts supported with forty metals; Na, K, Rb, Cs, Ca, Sr, Ba, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Zr, Mo, W, Sn, Pb, Bi, P, B, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. Four lines assigned to methyl radicals were newly observed on Na, Ca, Sr, Ti, Zn, Zr, Sn, Pb and Bi /SiO_2 as well as V, Mo and B/SiO_2 which were reported in the literature.[2,3]

Table 1 summarized hyperfine splittings of observed methyl radicals and effective wave length for photoactivation. Most of the methyl radicals seem to interact with metal ions or silica surface, since methyl radicals interacting with the solid surface are known to have smaller hyperfine splittings than ca. 23 G.[1] This is supported by the splitting of the radical, 22.7G, derived from CH_3I on SiO_2 as shown in the last row of Table 1.

Photo-illumination of vacuum UV such as wave length of ca. 125 nm was necessary for excitation of the methane molecule without catalyst.[9] Minimum photon energy estimated from C-H bond dissociation energy is ca. 280 nm (4.5 eV). Nevertheless, the samples listed in Table 1 give methyl radicals at wavelength higher than 250 nm. In particular, methyl radicals are formed even by the irradiation higher 280 nm on Na, Mg, V, Sr, Mo, Zn, Sn and B/SiO_2. Therefore, the solid surface plays an important role in photoactivation as well as stabilization of the free radicals. It seems that methane undergoes a photoassisted reaction through activation of solid surfaces. On Mo/SiO_2, Liu et al. have reported that O^- species are produced by charge transfer between the molybdenum ions and its lattice oxygen, and they subtracted hydrogen in methane[2] as follows.

$$Mo^{6+}O^{2-} \xrightarrow{h\nu} Mo^{5+}O^- \qquad (1)$$

$$Mo^{5+}O^- + CH_4 \longrightarrow Mo^{5+}OH^- + \cdot CH_3 \qquad (2)$$

Similar mechanism may be applicable to some cases of methyl radical formation in the present study. Detailed mechanistic elucidation is under investigation.

References and Notes

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