CHEMISTRY LETTERS, pp. 1723-1726, 1987.

Activation of Methane on the MgO Surface at Low Temperatures

Tomoyasu ITO,* Toshihiko TASHIRO, Tomoko WATANABE, Keio TOI, and Isao IKEMOTO
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukasawa, Setagaya-ku, Tokyo 158

The C-H bond of methane is easily activated on the MgO surface even below room temperature. Active sites consist of intrinsic ion pairs, O_{3C}^{2-}-Mg_{3C}^{2+} and O_{3C}^{2-}-Mg_{4C}^{2+}, of MgO in low coordination states on which a methane molecule adsorbs in heterolytically dissociated form.

Since methane has high molecular stability, the chemical utilization of natural gas which contains methane as the main component is a difficult and unsolved problem in today's industry. Hence activation of the C-H bond of methane is a current problem of great significance in heterogeneous catalysis. Recent studies have shown that the oxidative dimerization of methane to ethane and ethene over catalysts such as Sm_2O_3 and MgO is one of the most hopeful reaction to activate methane.1) This catalytic reaction, however, needs high reaction temperatures around 1000 K. It is desirable to find catalysts which can activate methane at lower temperatures.

Recent spectroscopic studies have directly revealed that coordinatively unsaturated ions are formed on the surfaces of MgO outgassed at high temperatures.2-4) These lowly coordinated ions has attracted special interest as a crystal imperfection responsible for surface properties of the oxide.4-6) This paper reports that a pair of surface ions of MgO with very low coordination numbers plays an important role in activating the C-H bond of CH_4 at low temperatures.

An MgO sample mainly used was obtained by the thermal decomposition in vacuo of a magnesium hydroxide sample, JRC-MgO-2, supplied from Catalysis Society of Japan. In a part of experiments another sample, MgO-JM, supplied from Johnson-Matthey Chemicals was also used. Adsorption behavior of methane on the two samples was qualitatively similar. The samples were outgassed at the prescribed pretreatment temperatures of 673-1123 K before each measurement and the same sample was repeatedly used through a series of measurements. The specific surface areas of the used catalysts were about 250 and 130 m^2g^{-1} for JRC-MgO-2 and MgO-JM, respectively. All the gases used were of high purity. TPD spectra were measured in a vacuum system equipped with a quadrupole mass spectrometer.

Figure 1 shows TPD spectra of CH_4 adsorbed on the MgO surface pretreated at various temperatures. These were measured after the admission of 1.3 kPa of CH_4 onto the sample at room temperature followed by a gradual cooling to 77 K in the presence of the gas. The concentration of active sites for methane adsorption rapidly increases with increasing pretreatment temperature. TPD spectrum for the sample pretreated at the highest temperature of 1123 K (curve d) exhibits three peaks; main one designated M_{1A} with desorption maximum at 300 K and two sub-peaks, M_{1B} and M_{1C}, desorbing at 370 and 450 K, respectively. Adsorption was scarcely observed on the samples pretreated below 823 K.

The pretreatment-temperature dependence described above strongly suggests that the adsorption sites for the M_1 species consist of low-coordination surface ions since these ions also increases in concentration with increasing pretreatment temperature.[2)] To confirm this point we examined poisoning effect of hydrogen on

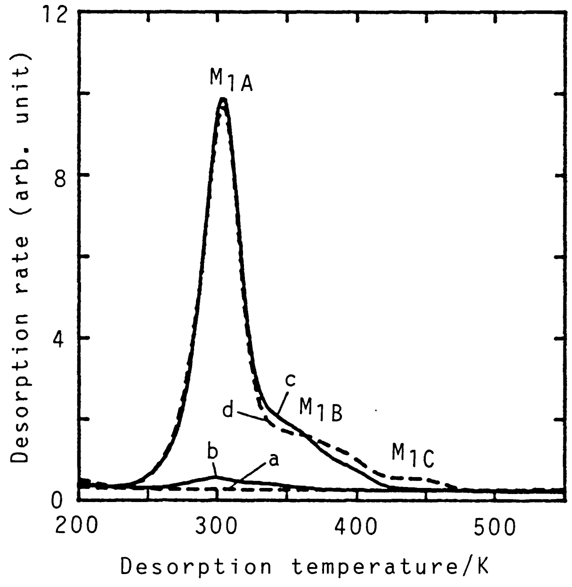

Fig.1. TPD of methane adsorbed on JRC-MgO-2 pretreated at (a)673, (b)823, (c)973, and (d)1123 K, respectively.

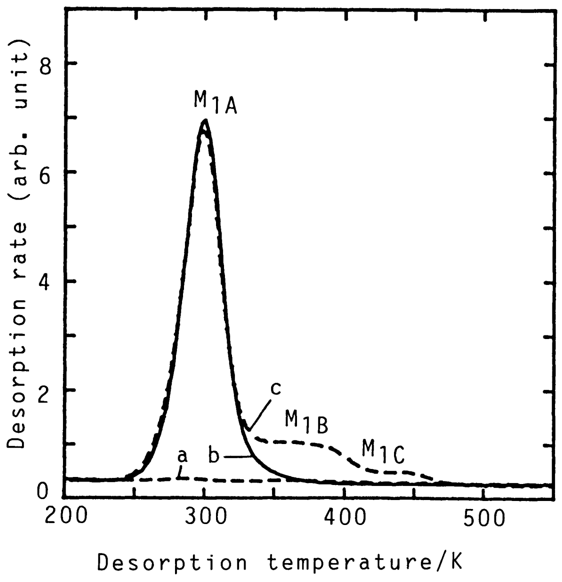

Fig.2. TPD of methane adsorbed on JRC-MgO-2 carrying preadsorbed hydrogen species (a)W_5-W_8, (b)W_6-W_8, and (c)nothing, respectively.

the methane adsorption. Seven types of active sites for the hydrogen adsorption on MgO were found by TPD measurements in our previous work and labeled as W_2 to W_8 in the order of increasing peak temperature.[5)] Figure 2 shows poisoning effects observed on the sample pretreated at 1123 K where specified species of preadsorbed hydrogen were formed by the adsorption of hydrogen at 273 K followed by desorbing unnecessary preadsorbed species by heating under evacuation. Curves (a) and (b) were observed when 1.3 kPa of methane was introduced below 253 K to the samples which had been already covered by preadsorbed hydrogen species W_5-W_8 and W_6-W_8, respectively, while curve (c) was observed on the surface without any preadsorbed hydrogen. All the active sites M_1 for methane were completely blocked by the preadsorbed hydrogen of species W_5-W_8. The M_{1A} site, however, was completely recovered on the surface carrying preadsorbed species W_6-W_8 only, but the M_{1B} and M_{1C} sites were not at all. The surface concentration of the total M_1 sites, estimated from the TPD area, is approximately equal to that of the W_5-W_8 sites; they are only about 50 ppm of the number of total surface ions for JRC-MgO-2. Similarly the presence of the preadsorbed M_1 species also blocked the adsorption of hydrogen as species W_5-W_8. These facts clearly demonstrate that the M_{1A} site and the M_{1B} and M_{1C} sites for methane are identical to the W_5 site and the W_6-W_8 sites for hydrogen, respectively. The structures of the W_5 and the W_6-W_8 sites have been already revealed by us[5)] and others[4,6)] to be anion-cation pairs with low coordination number, O_{3C}^{2-}-Mg_{4C}^{2+} and O_{3C}^{2-}-Mg_{3C}^{2+}, respectively, where the subscript denotes a coordination number.

Figure 3 shows an ESR spectrum observed after the admission of 1.3 kPa of oxygen onto the sample surface on which the M_1 sites had been already covered by preadsorbed methane. This spectrum clearly demonstrates the formation of superoxide ions, O_2^-, on the surface carrying the M_1 species; there are at least three kinds of O_2^- with g_z components at 2.093, 2.081, and 2.074, respectively. This formation of O_2^- indicates that methane is adsorbed in a

Fig.3. ESR spectrum of O_2^- formed on MgO-JM pretreated at 1123 K.

heterolytically dissociated form, H^+ and CH_3^-, as the M_1 species since this criterion has been justified in other hydrogen-containing molecules such as hydrogen and ethene.6-8) Upon the admission of oxygen onto the bare surface O_2^- was not formed.

This study has shown that MgO catalysts can easily activate the C-H bond of methane at low temperatures. Indeed the M_1 species can be formed even at 223 K. The structures of the active sites and of the adsorbed species have also been revealed, and these findings may lead to new possibilities to use natural gas chemically at low temperatures. It is not clear, at the present stage, whether the M_1 species participates in the oxidative dimerization reaction at high temperatures. It has been known that aluminum oxide also can activate methane at room temperature;9) in this case, however, active sites and adsorption states have not been clear.

References

1) T. Ito, J.-X. Wang, C.-H. Lin, and J. H. Lunsford, J. Am. Chem. Soc., 107, 5062 (1985); T. Moriyama, N. Takasaki, E. Iwamatsu, and K. Aika, Chem. Lett., 1986, 1165; K. Otsuka, Q. Liu, M. Hatano, and A. Morikawa, Chem. Lett., 1986, 903; H. Imai and T. Tagawa, J. Chem. Soc., Chem. Commun., 1986, 52.

2) A. Zecchina, M. G. Lofthouse, and F. S. Stone, J. Chem. Soc., Faraday Trans. 1, 71, 1476 (1975).

3) E. Garrone, A. Zecchina, and F. S. Stone, Philos. Mag. Part B, 42, 683 (1980).

4) S. Coluccia and A. J. Tench, "Proc. 7th Intern. Congr. Catal.," Kodansha-Elsevier, Tokyo (1981), p. 1154.

5) T. Ito, M. Kuramoto, M. Yoshioka, and T. Tokuda, J. Phys. Chem., 87, 4411 (1983).

6) E. Garrone and F. S. Stone, "Proc. 8th Intern. Congr. Catal.," Verlag Chemie, Weinheim (1984), Vol. 3, p. 441.

7) T. Ito, M. Yoshioka, and T. Tokuda, J. Chem. Soc., Faraday Trans. 1, 79, 2277 (1983).

8) V. Indovina and D. Cordischi, Chem. Phys. Lett., 43, 485 (1976).

9) J. G. Larson and W. K. Hall, J. Phys. Chem., 69, 3080 (1965); M. Utiyama, H. Hattori, and K. Tanabe, J. Catal., 53, 237 (1978); L. Quanzhi and Y. Amenomiya, Appl. Catal., 23, 173 (1986).

(Received May 30, 1987)