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Oxidative Coupling of Methane over Ultrafine Crystalline MgO Doped with Li. Role of Lower Coordinative Surface Sites Produced by Li-doping

Masakazu ANPO,* Masatoshi SUNAMOTO, Takao DOI,+ and Ikuya MATSUURA+
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591
+Department of Chemistry, Faculty of Science,
Toyama University, Gofuku, Toyama, Toyama 930

A good parallel between the intensity of newly observed photoluminescence at around 450 nm with Li-doped MgO catalysts and their activity for oxidative coupling of methane was found, indicating that lower coorinative surface sites produced by incorporation of Li into MgO play a significant role in methane oxidative coupling.

Oxidative coupling reaction of methane to form higher hydrocarbons has been studied with various oxidic systems, from the standpoint of a potential route for methane conversion.1-7) Among them, MgO doped with alkaline metal ions such as Li^+ (with content of 10-40 mol%) is one of the most prospective and widely studied systems.1,4) Recently, we have found that the ultrafine crystalline MgO doped with Li of only 1-5 mol% exhibits extremely high activity for the oxidative coupling of methane to C_2-hydrocarbons. However, there are few works to study the nature of the active sites for the oxidative coupling of methane.1)

Measurements of the photoluminescence spectra of MgO catalysts in their intensity and shapes give useful information about physicochemical properties of MgO surfaces with coordinatively unsaturated surface sites which play a significant role in the catalytic activity of MgO.8,9) Therefore, it is of special interest to investigate the surface active sites on the highly active MgO catalysts doped with a small amount of Li by using highly sensitive and non-destructive photoluminescence techniques. We now report the relationship between the photoluminescence properties and the activity of Li-doped MgO catalysts for the oxidative coupling of methane.

The Li-added MgO catalysts were prepared as follows; a specified quantity of Li_2CO_3 (Wako Chem. Co., purity $\gg$99.0%) was added to a suspension of commercial MgO microcrystals (Ube #500, purity$\gg$99.9%, BET surface area; 25— 40 m^2/g) in distilled water. The dried substance was calcined at 1073 K for 2 h. X-Ray diffraction measurements showed that the undoped original MgO samples had pure single crystal structure with particle size of 450— 600 A, though those were reconstructed by the addition of Li_2CO_3, to an extent depending on the amount of Li_2CO_3, accompanied by a concomitant reduction of their surface area. Photoluminescence spectra of the catalysts were measured at 77 and 298 K with a Shimadzu RF-501 spectrofluorophotometer equipped with colour filters. The catalytic reactions were carried out in a fixed bed reactor at a constant flow rate, 250 ml/min of the mixed gas of CH_4, O_2, and He under the total pressure of one atmosphere (101.3 kPa).[5)]

Figure 1 shows the catalytic activity of Li-doped MgO catalysts for the oxidative coupling reaction of methane under the condition of the partial pressures of 35 kPa of CH_4 and 16.5 kPa of O_2 at 953 K. As shown in Fig. 1, the undoped original MgO catalyst exhibits only much lower activity for the reaction with lower selectivity for the formation of C_2-compounds (C_2H_6 and C_2H_4). With Li-doped MgO catalysts, both the yields and the selectivity for C_2-compounds formation remarkably increase with increasing amount of Li added to MgO. An optimum activity is seen with 3 mol% Li-MgO. When the amount of Li exceeds more than 5 mol%, catalytic activity decreases, to an extent depending on the amount of Li added. Together with the fact that selectivity for C_2-compounds formation increases first and then becomes constant to be 55% for the cata-

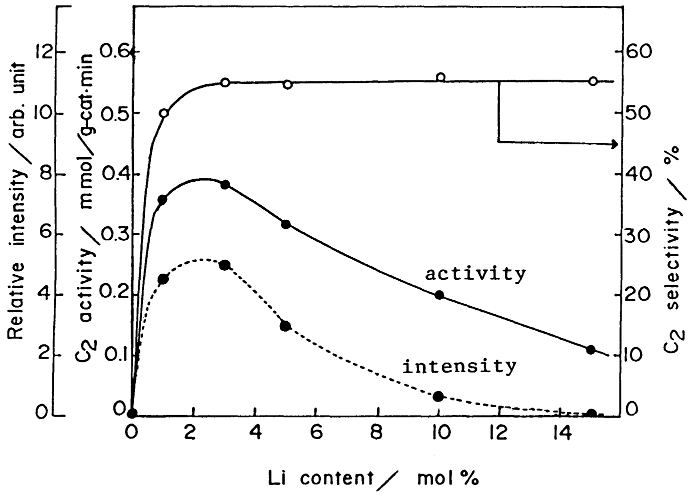

Fig. 1. Effects of Li-doping upon the activity and the selectivity of methane coupling reactions, and the intensity of newly observed photoluminescence at around 420-520 nm
(temperature: 965 K for catalytic reaction; 77 K for photoluminescence measurement, excitation: 240 nm, selectivity: for C_2-compounds formation)

lysts with the content of more than 3 mol% of Li, such a decrease in the catalytic activity might be attributed to a reduction of the surface area of the catalysts.

As shown in Fig. 2, an undoped MgO sample which had been degassed at the same temperature to the reaction exhibits a characteristic photoluminescence spectrum (solid line (1)) having λ_{max} at around 360 nm. Its excitation band was observed at around 220– 270 nm, being associated with the following (equation (1)) charge transfer processes on the coordinatively unsaturated surface sites with the coordination number of four.[8,9)

$$(Mg^{2+} — O^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (Mg^{+} — O^{-})^{*} \qquad (1)$$

Figure 2 shows the photoluminescence spectrum of the 3 mol% Li- MgO catalyst and its deconvoluted spectra. In addition to a characteristic emission for pure MgO (dotted line (2-a)), Li-doped MgO catalyst exhibits a new emission having λ_{max} at around 450 nm (dotted line (2-b)), to an intensity depending on the amount of Li added to MgO. The excitation spectrum of this new emission was observed at around 260– 290 nm. According to the previous papers,[8,9) the lower coordinative surface sites than those with coordination number of four may be associated with this new photoluminescence, because the lower the coordination, the lower the energy becomes.

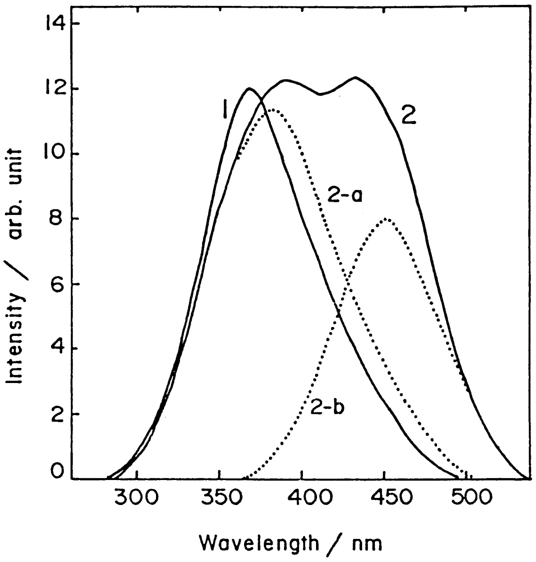

Fig. 2. Photoluminescence spectra of MgO (solid line (1)), and of 3 mol% Li doped MgO (solid line (2)) and its deconvolued spectra (dotted lines (2-a) and (2-b))
(excitation wavelength: 240 nm, recording range: 500 mV for line (1), 200 mV for line (2))

As shown in Fig. 1, increasing the amount of Li added, the intensity of the newly observed photoluminescence increases, passing through a maximum at the amount of added Li of 3 mol%, and then decreases. A good parallelism between the intensity of newly observed photoluminescence at around 450 nm and the activity of Li-doped MgO catalysts for the methane coupling reaction suggests that newly produced unsaturated surface sites with coordination number lower than four play a significant role in the oxidative coupling reaction of methane.

The addition of CH_4 at 0.1 Torr onto the 3 mol% Li-doped MgO at 298-573 K scarcely quenched the photoluminescence. However, the addition of CH_4 at the temperature above 723 K onto the Li-doped MgO led to quenching the newly observed photoluminescence, but still did not quench a characteristic emission at around 320-420 nm. A characteristic photoluminescence was quenched with CH_4 only at the temperature above 873 K. These quenching results imply that the reactivity of newly produced unsaturated surface sites by incorporation of Li is much higher than that of original unsaturated surface sites on undoped pure MgO. This might be linked with the fact that the lower the coordination number becomes, the higher the activity of unsatuatred surface sites is.[8,9)

Lunsford et al.[1) have detected (Li^+-O^-) and O^- sites on Li-promoted MgO (7 Li mol%) by EPR, suggesting that these sites play a singificant role in the formation of $\dot{C}H_3$ radicals from CH_4. It is not clear at the present whether newly produced lower coordinative surface sites are directly associated with an existence of the sites detected by Lunsford et al.[1) or not. However, high activity of the present catalysts involving a small amount of Li seems to be better agreement with the formation of lower coordinative surface sites, because un-doped pure MgO also exhibits an activity for the oxidative coupling of methane, its reactivity being much lower than those of Li-doped MgO catalysts (Fig. 1).

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