Lithium-doped sulfated-zirconia catalysts for oxidative coupling of methane to give ethylene and ethane

Kazuhisa Murata[*], Takashi Hayakawa, Satoshi Hamakawa, Kunio Suzuki

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

Abstract

Li-doped sulfated-zirconia catalysts were found to be effective for oxidative coupling of methane (OCM). The catalyst performances depend on the sulfate content and calcination temperature. A maximum C_2 yield is attained over the catalysts, which contain 6 wt.% sulfate and calcined at 923–973 K, being closely related to the preparation conditions of sulfated-ZrO_2 as solid super-acids. When the performances of the Li-doped sulfated-ZrO_2 (Li/SZ) catalysts were tested at 1023 K as a function of reaction time, both the C_2 and CO_x selectivities remained constant over the range of 8 h, but the CH_4 conversion decreased from 17.5% to 11.9%. The nature of Li/SZ catalysts for the OCM was investigated by X-ray diffraction, XPS, and NH_3 and CO_2 TPD measurements. It could be postulated that the sulfated-ZrO_2 surface could play an important role in the formation of a catalytically active structure by Li-doping. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In this decade, much attention has been paid to the conversion of methane into more valuable products under oxidative [1] or non-oxidative [2] conditions. Of many attempts, oxidative coupling of methane (OCM) to give C_2 hydrocarbons is still one of the promising choices for the direct methane conversion. Generally, research efforts have been directed towards a search for new efficient catalysts and basic metal oxides such as MgO, CaO, and La_2O_3 are mostly used as catalysts or supports. However, it seems likely that the strong basicity of catalysts used are always not required [3].

In the present work, the effectiveness of lithium-doped sulfated-zirconia catalyst systems on the OCM

reaction was examined and the systems were found to be excellent novel candidates for the C_2 formations. Now we wish to report some of our results.

2. Experimental

The catalysts were prepared as follows [4]: Amorphous zirconia (AZr) was first synthesized by hydrolyzing an aqueous $ZrO(NO_3)_2$ solution with ammonia, followed by calcination for 3 h at 573 K. Then, the resulting AZr (B.E.T. surface area=266 $m^2 g^{-1}$) was added to $(NH_4)_2SO_4$ solution and evaporated to dryness, accompanied by calcination in air for 3 h at 973 K. The resultant sulfated-zirconia (SZ, 72.8 $m^2 g^{-1}$) was impregnated with an aqueous solution of Li_2CO_3. This was then evaporated to dryness, drying overnight at 373 K, calcination in air at 873 K for 3 h,

*Corresponding author. Tel.: +81-298-54-4774; fax: +81-298-54-4487; e-mail: kazumutata@ccmail.nimc.go.jp

to form Li-doped sulfated-zirconia (Li/SZ, 7.3 m^2 g^{-1}). Zirconia catalyst (Zr) was prepared by calcinating AZr for 3 h at 973 K. Also, Li-doped zirconia catalyst (Li/Z) was obtained by impregnation of AZr with an aqueous solution of Li_2CO_3, followed by calcination in air at 873 K for 3 h.

The catalytic runs were carried out under atmospheric pressure and in a fixed bed vertical flow reactor constructed from a high purity alumina tube (i.d. 6 mm) packed with 0.5 g of catalyst and mounted inside a tube furnace. The catalyst was pretreated in nitrogen at 1073 K for 1 h then, the reactant gas mixture was introduced at W/F=4.1 g-cat h mol^{-1}. The products were analyzed on-line by gas chromatography (GC). XRD patterns of catalysts were recorded with a Philips PW1800 diffractometer using CuKα radiation (λ=0.1538 nm). Temperature-programmed desorption experiments were carried out using a NH$_3$/CO$_2$-TPD apparatus (Ohkura Riken) interfaced to a personal computer. TPD profiles were obtained under vacuum conditions. The temperature was increased from 373 to 773 K at a rate of 10 K min^{-1} for NH$_3$ and from 303 to 773 K for CO$_2$. The amount of NH$_3$ or CO$_2$ evolved was determined with a thermal conductivity detector (TCD). X-ray photoelectron (XPS) spectra was recorded on a PHI-5500 using monochromatized Al Kα radiation (1486.6 eV).

3. Results and discussion

3.1. Preliminary study on catalytic activity

The major products of the oxidative coupling of methane are C$_2$ (ethylene, ethane and acetylene), carbon monoxide and carbon dioxide with only trace amount of C$_3$ (propane, propylene, and propyne), C$_4$ and C$_5$ mixtures and aromatics (benzene and toluene). The results obtained in the various ZrO$_2$ catalysts at 1073 K are presented in Fig. 1. In the Zr and SZ catalysts, some reaction took place, carbon oxides being, however, the dominant products and C$_2$ compounds in only 3% yield. For Li/Z catalyst without sulfate, the CH$_4$ conversion was almost unaltered, but C$_2$ selectivity (ca. 33.8%) improved slightly. On the contrary, a clear improvement in C$_2$ selectivity (60.9%) were observed at 31% CH$_4$ conversion over Li/SZ catalyst: This is the first example of the use of
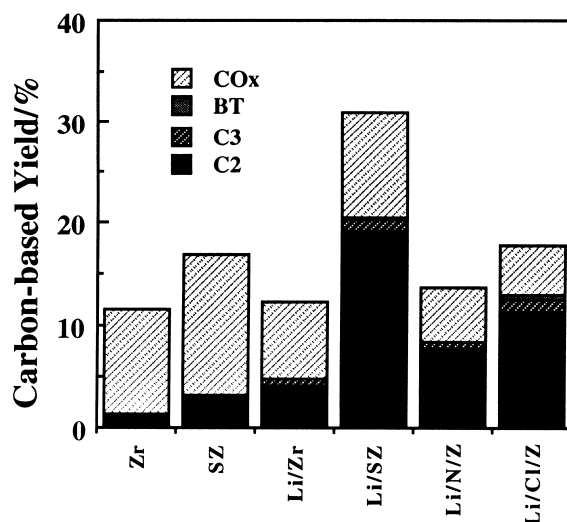

Fig. 1. The OCM reaction over various ZrO$_2$ catalysts. Reaction temperature: 1073 K. Gas composition: CH$_4$/O$_2$/N$_2$=15/5/80. Catalysts: Zr, SZ, Li/Z, Li/SZ; see text. Li/N/Z:Li/(NH$_4$)NO$_3$/ZrO$_2$. Li/Cl/Z:Li/(NH$_4$)Cl/ZrO$_2$.

solid-super-acid-based catalysts for the oxidative coupling of CH$_4$ [1].

3.2. Effect of reaction temperature

Fig. 2 shows the effects of reaction temperature on the OCM reaction, where the Li/SZ catalyst was used. The CH$_4$ conversion increased with the increase in reaction temperature, whereas the C$_2$ selectivities
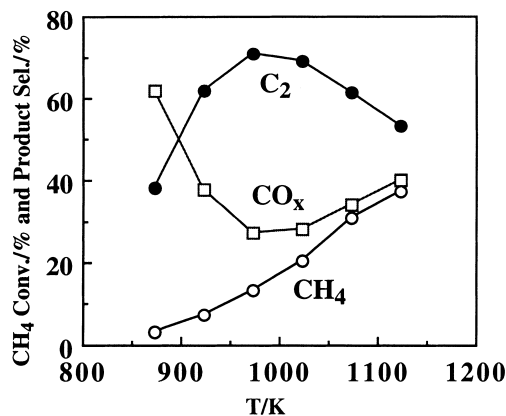

Fig. 2. Temperature dependence on the OCM reaction. Catalyst: Li/SZ. Gas: CH$_4$/O$_2$/N$_2$=15/5/80.

increased with the increase in the temperature and levelled off at 1023 K, then, decreased with the temperature increase. The findings in the temperature below 1000 K could be explained by the view that the activation energy of C_2 formation is of second order for CH_3 radicals, whereas that of CO_x formation is of first order reactions [5]. Also, the decrease in C_2 products above 1000 K would be accounted for by successive reaction of the C_2 to form CO_x.

3.3. Effects of catalyst components and preparation conditions

In order to examine the effect of catalyst components, catalysts prepared using other acid sources and other alkali metals were tested. The Li-doped acid-promoted ZrO_2 catalysts, which was prepared by impregnation of acid precursors (6 wt.%), were also effective for this reaction; The C_2 yield at 1073 K was in the order: $(NH_4)_2SO_4$ (19.0)$\cong$ 1 N H_2SO_4 (19.0)> NH_4Cl (11.33)> trimethylene borate (10.5)> $(NH_4)_3$ PO_4 (9.12)> NH_4NO_3 (7.80)> none (4.13). For the Na- and K-doped sulfated-ZrO_2 catalysts, the C_2 yields were lower than that for Li/SZ catalyst. For catalysts promoted with 10 wt.% of Li, both CH_4 conversion and C_2 selectivity slightly reduced and, as a result, the C_2 yield decreased down to ca. 14%. The catalyst performances depend on the sulfate content (Fig. 3) and calcination temperature (Fig. 4). A maximum C_2 yield was attained over the catalysts, which contain 6 wt.% sulfate and calcined at 923–973 K, although
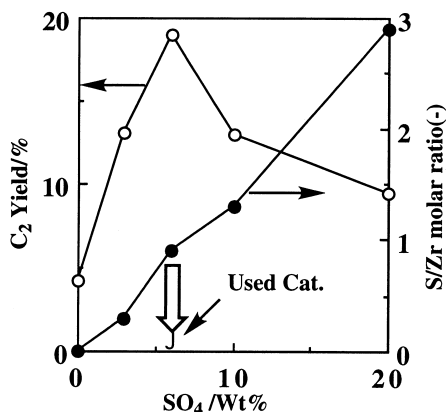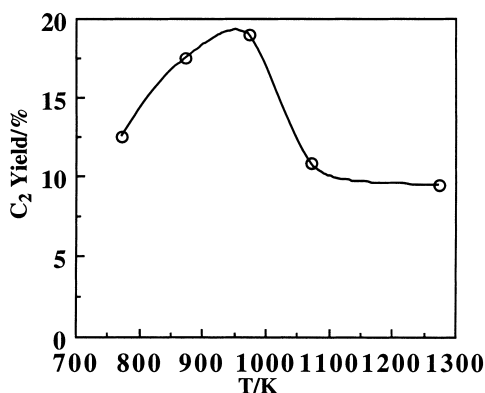
Fig. 4. Effect of calcination temperature of SZ. Reaction temperature: 1073 K.

the peak intensity ratio of S_{2p}/Zr_{3d}, evaluated from XPS measurements, increased linearly with the sulfate loading in the range of 0–20 wt.% $(NH_4)_2SO_4$ (Fig. 3($\bullet$)). These findings seem to be associated with the preparation conditions of sulfated-ZrO_2 as solid super-acid [6].

3.4. X-ray diffraction data

The zirconia support calcined at 573 K was amorphous as shown by the XRD pattern given in Fig. 5(a). The S/Z catalyst exhibited the XRD pattern for tetragonal phase with a small amount of monoclinic phase (Fig. 5(b)) and the Li/Z catalyst revealed only a tetragonal phase (Fig. 5(c)). On the contrary, in case of the Li/SZ catalyst, clear Li_2ZrO_3 phases (monoclinic and tetragonal) were observed with the zirconia phases (monoclinic and tetragonal) (Fig. 5(d)). At this time, it is not clear whether mixed-oxide phases could be catalytically active structures or not. However, it seems likely that the sulfated-ZrO_2 surface could play an important role in the formation of a catalytically active structure by Li-doping.

3.5. NH_3 and CO_2 TPD data

Fig. 6(a) display NH_3 TPD profiles of Li/Z and Li/SZ catalysts. The presence of one peak was observed at 490–550 K. Unexpectedly, an amount of NH_3 desorbed was very small and there was little difference between Li/Z and Li/SZ catalysts, although the desorption temperature for Li/SZ was slightly higher than
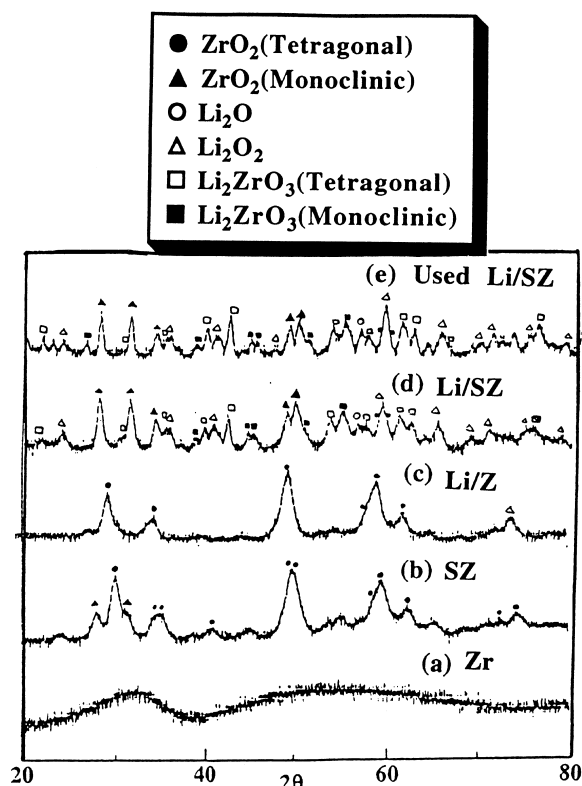
Fig. 3. Effects of sulfate content on the C_2 yield and S_{2p}/Zr_{3d} molar ratio.

Fig. 5. X-ray diffraction patterns for various sample: (a) ZrO_2; (b) 6 wt.% SO_4/ZrO_2 (SZ); (c) 5 wt.% Li/ZrO_2 (Li/Z); (d) 5 wt.% Li/ 6 wt.% SO_4/ZrO_2 (Li/SZ); (e) used Li/SZ after 8 h-reaction.

Table 1
NH_3 and CO_2 TPD data[a]

Catalyst	NH_3 TPD Desorption temperature (K)/ amount (mmol)	CO_2 TPD Desorption temperature (K)/ amount (mmol)
Li/Z	497/0.063	347/0.26
		549/1.03
Li/SZ	549/0.038	379/0.13
		586/1.13

[a] TPD conditions: See text.

that for Li/Z (Table 1). Then, CO_2 TPD measurement was performed using these catalysts. As shown in Fig. 6(b), two peaks were observed, peak I at 340–380 K and peak II at 540–590 K. Again, the behaviors of CO_2 desorption for Li/SZ were similar to those for Li/Z and the CO_2 desorption temperature was slightly
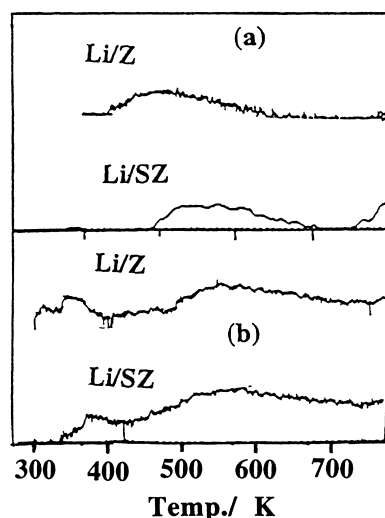

Fig. 6. Temperature-programmed desorption (TPD) profiles of NH_3 (a) and CO_2 (b) from the Li/Z and Li/SZ catalysts.

higher for Li/SZ than that for Li/Z. The amount of CO_2 desorption (0.1–0.3 mmol/g (peak I) and 1.0–1.2 mmol/g (peak II)) was larger than that of NH_3 desorption (0.04–0.06 mmol/g). Thus, acid–base property of Li/SZ surface was found to be approximately analogous to that of Li/Z, indicating that the Li/SZ surface could not be of a super-acid character, due to, at least, partially neutralization by impregnation of Li_2CO_3.

3.6. Catalyst performances as a function of time

The reaction using Li/SZ catalyst was carried out at 1023 K under a mixed gas flow of $CH_4/O_2/N_2$ (=10/5/80). Both the C_2 and CO_x selectivities remained constant over the range of 8 h, but CH_4 conversion decreased (Fig. 7(○), 17.5%→11.9%). At this point, the X-ray diffraction of the used Li/SZ catalyst exhibited a pattern similar to the fresh catalyst (Fig. 5(e)). However, the surface sulfate content of the used Li/SZ was dramatically decreased, as confirmed by the comparison of the XPS peak intensity ratio of S_{2p}/Zr_{3d} of the used Li/SZ with that of the fresh catalyst (Figs. 3 and 8). Therefore, likely, a surface structure of Li/SZ was varying as the reaction proceeded.

In summary, Li-doped sulfated-zirconia (Li/SZ) catalysts were found to be effective for (OCM). The catalyst performances depend on the sulfate content
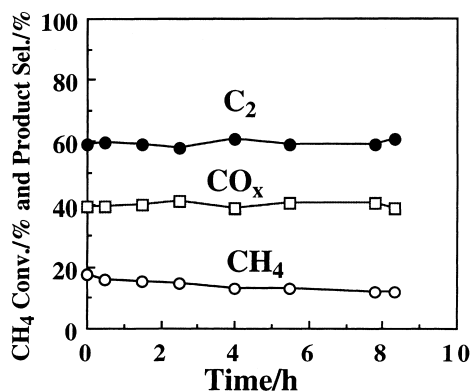
Fig. 7. Catalytic activity as a function of time in the OCM reaction. Catalyst: Li/SZ. Gas: $CH_4/O_2/N_2 = 10/5/85$.

Fig. 8. XPS Spectra of S_{2p} of the fresh and used catalyst. Catalyst: Li/SZ. Used: after 8 h-reaction.

and calcination temperature. A maximum C_2 yield is attained over the catalysts, which contain 6 wt.% sulfate and calcined at 923–973 K. When the performances of the Li/SZ catalysts were tested at 1023 K as a function of reaction time, both the C_2 and CO_x selectivities remained constant over the range of 8 h, but the CH_4 conversion decreased from 17.5% to 11.9%. The nature of Li/SZ catalysts for the OCM was investigated by X-ray diffraction, XPS, and NH_3 and CO_2 TPD measurements. The Li/SZ surface could not be of super acidic character, due to, at least, partial neutralization by impregnation of Li_2CO_3. Therefore, the temperature range required for the catalyst system is almost the same as that for basic catalysts such as Li/MgO (Fig. 2) [1]. It could be postulated that the sulfated-ZrO_2 surface could play an important role in the formation of a catalytically active structure by Li-doping, since the zirconia catalyst, prepared from
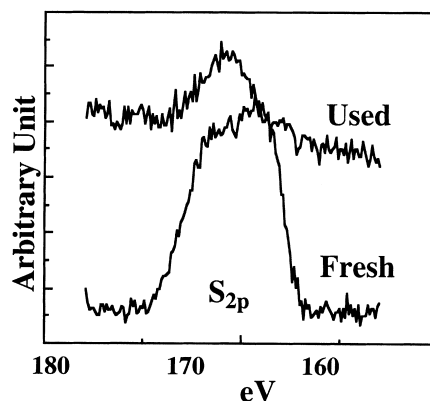
an aqueous solution containing both $(NH_4)SO_4$ and Li_2CO_3, was having much lower reactivity than that prepared by two-step methods.

Further work is in progress to improve the catalyst performances.

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