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Oxidative coupling of methane over Ba-doped Y₂O₃ catalyst—Similarity with active site for direct decomposition of NOMasaaki Haneda^{a,b,*}, Makoto Tanaka^a, Yasuyuki Doi^{a,b}, Nicolas Bion^c^a Advanced Ceramics Research Center, Nagoya Institute of Technology, 10-6-29 Asahigaoka, Tajimi, Gifu 507-0071, Japan^b Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Gokiso-cho, Showaku, Nagoya 465-8555, Japan^c Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), University of Poitiers, CNRS, UMR 7285, 4 rue Michel Brunet - TSA 51106 - 86073 Cedex 9, France

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ABSTRACT

A similarity of catalytically active sites for oxidative coupling of methane (OCM) and NO decomposition was investigated. Y₂O₃ prepared by different methods showed the activity for both reactions. However, no good correlation between the C₂ (C₂H₆ and C₂H₄) yield for the OCM reaction and the NO decomposition activity was observed. Since the disagreement of the catalytic activity for both reactions was suspected to be due to the non-uniform surface morphological properties of Y₂O₃, detail experiments were performed for Ba-doped Y₂O₃ catalysts. It was noteworthy that the addition of Ba into Y₂O₃ prepared by precipitation method caused a significant increase in not only the C₂ yield for the OCM reaction but also the NO decomposition activity. The order of the C₂ yield for the OCM reaction over Ba/Y₂O₃ with different Ba loading was in good agreement with that for the NO decomposition, suggesting the similarity of the active sites for the OCM and NO decomposition reactions. XRD, FT-IR spectroscopy following methanol adsorption and ¹⁶O/¹⁸O isotopic exchange reaction revealed that the oxygen-deficient Y³⁺ sites interacting strongly with Ba play a beneficial role in O₂ activation, leading to the activation of CH₄ and NO molecules to form intermediate in the OCM and NO decomposition reactions.

1. Introduction

Methane, which is the main constituent of natural gas, is an abundant hydrocarbon resource for energy and chemicals. Among the methane conversion technologies to the chemicals, oxidative coupling of methane (OCM) is regarded as energy efficient and simple chemical process for the production of higher hydrocarbons, especially, ethane and ethylene [1]. The development of highly active OCM catalyst has been continuously performed over the past few decades [2–4] since the pioneering works of Keller and Bhasin [5] and Hinsen and Baerns [6].

The OCM reaction proceeds via the formation of methyl (CH₃) radicals formed by the reaction of methane with active oxygen species and subsequent coupling the methyl radicals [7]. Methane is, however, the most stable hydrocarbon, leading to the difficulty of its selective activation to form CH₃ radical intermediate, so that designing the catalyst surface to create the active oxygen species such as O[•], O₂²⁻ and O²⁻ for the OCM reaction must be the important strategy to develop highly active catalysts. As for the initial work, Lunsford et al. clarified the participation of O[•] species formed on [Li⁺O⁻] center in the formation of methyl radicals for the OCM reaction over Li/MgO [8,9]. Buyevskaya et al. [10] investigated the isotopic oxygen exchange

reaction over Sm₂O₃/MgO under the transient conditions, and revealed that the oxygen activation on the surface is faster than activation of methane and the surface oxygen species, *O_(s), formed via dissociative adsorption, are highly reactive toward methane activation.

The research group of Baerns et al. [11,12] has recently analyzed past catalytic data on the OCM reaction in order to gain new insights into the composition of high-performance catalysts. They revealed that all oxides of the selected elements, which positively affect the selectivity to C₂ products, show strong basicity, and that binary and ternary oxides showing high performance are mainly based on Mg and La oxides. Alkaline (Cs, Na) and alkaline earth (Sr, Ba) metals are also effective dopants to increase the C₂ selectivity of the host oxides. Okabe et al. [13] reported a good correlation between the surface basicity and C₂ selectivity for the OCM reaction over SrO-La₂O₃ catalysts, where the surface basicity was correlated with the binding energy difference between La 3d and O 1s levels of the catalysts. The productivity of the catalytic systems composed of basic oxides seems to be attributed to the availability of oxygen vacancies and/or other defects as active sites, which are important for oxygen activation [14–16].

Boreskov [17] measured the catalytic activity of the 4th period transition metal oxides for various catalytic reactions such as NO

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decomposition, methane oxidation and hydrogen oxidation, and revealed a distinct similarity in the change of a specific catalytic activity of metal oxides with respect to the above reactions. This may be due to the similarity of an essential contribution to the energy of an active complex, in this case, active oxygen species. The catalyst showing the activity for one reaction may also be effective for other reaction, if the characteristics of catalytically active sites for each reaction are similar.

We have extensively studied the catalytic activity of Ba-doped Y_2O_3 for the direct decomposition of NO, and revealed the close correlation between the surface basicity and the catalytic activity of Ba/ Y_2O_3 [18–21]. In accordance with the case of the OCM reaction, oxygen vacancies and/or other defects related to the surface basicity were suggested to act as active sites in NO decomposition. On the basis of *in situ* FT-IR spectroscopy and isotopic transient kinetic analysis, a reaction scheme in which NO_2^- intermediate can be formed *via* the activation of NO molecule with active oxygen species created on basic site was proposed [21–23]. A similar role of basic sites in Ba-doped C-type cubic Y_2O_3 -ZrO₂ for NO decomposition was also reported by Tsujimoto et al. [24]. It can be expected that the active catalysts for NO decomposition are also active for the OCM reaction.

In this study, we particularly addressed Y_2O_3 -based catalyst, which shows the activity for the OCM and NO decomposition reactions [18,25–27], and then investigated the similarity of catalytic performance of Ba-doped Y_2O_3 for both reactions. We also performed $^{16}O/^{18}O$ isotopic exchange reaction to understand the difference in the catalytic performance of Ba-doped Y_2O_3 . We want to propose new insights into the strategy for producing the OCM catalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Y_2O_3

A plural Y_2O_3 catalyst was prepared by precipitation, reverse precipitation, homogeneous precipitation and hydrothermal methods. The details of Y_2O_3 catalysts prepared in the present study are summarized in Table 1.

(A)

(A) *Precipitation method ($Y_2O_3(P)$)*: To an aqueous solution of yttrium(III) nitrate ($Y(NO_3)_3 \cdot 6H_2O$, Wako Pure Chemical Industries) was added an aqueous solution of ammonia (10% NH_4OH , Wako Pure Chemical Industries) as a precipitation agent at room temperature. The precipitate thus obtained was washed with distilled water, followed by drying and calcination at 600 °C for 5 h in air.

(B) *Reverse precipitation method ($Y_2O_3(RP)$)*: To an aqueous solution of ammonia as a precipitation agent was added an aqueous solution of yttrium(III) nitrate at room temperature. The precipitate thus obtained was washed with distilled water, followed by drying and calcination at 600 °C for 5 h in air.

(C) *Homogeneous precipitation method ($Y_2O_3(HP)$)*: The precipitation of yttrium hydroxide was obtained by adding urea ($CO(NH_2)_2$, Wako Pure Chemical Industries) to an aqueous solution

of yttrium(III) nitrate and stirring at 90 °C for 24 h, and then washed with distilled water, followed by drying and calcination at 600 °C for 5 h in air.

(D) *Hydrothermal method ($Y_2O_3(HT)$)*: The oleate solution prepared by dissolving potassium oleate ($C_{17}H_{33}COOK$, 19% solution, Wako Pure Chemical Industries) with distilled water was added to an aqueous solution of yttrium(III) nitrate at room temperature under vigorously-stirred condition, followed by addition of ammonia aqueous solution. The mixture solution thus obtained was transferred to a Teflon vessel and then treated at 200 °C for 48 h in an autoclave. The product thus obtained was washed with distilled water, followed by drying and calcination at 600 °C for 5 h in air.

2.1.2. Ba-doped Y_2O_3

Ba-doped Y_2O_3 was prepared by impregnating Y_2O_3 powder, which was obtained by precipitation method as mentioned above, with an aqueous solution of barium(II) nitrate ($Ba(NO_3)_2$, Wako Pure Chemical Industries), followed by drying and calcination at 600 °C for 5 h in air. The loading of Ba was changed from 0.5 to 15 wt%.

2.2. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex diffractometer with Cu K α radiation at 30 kV and 15 mA. The scanning was done from $2\theta = 15$ –65 ° at a speed of 1 deg min⁻¹. The BET surface area of the catalysts was determined by N₂ physisorption at liquid nitrogen temperature using a BELSORP mini-II, after evacuating the samples at 300 °C for 1 h. Fourier transform infrared (FT-IR) spectra of adsorbed methanol as a probe molecule were taken to characterize the coordination status of surface Y³⁺ cations. A self-supporting sample disk of about 20 mg cm⁻² placed in an IR cell with CaF₂ windows was first activated at 600 °C for 1 h with oxygen at 40.0 kPa and then evacuated at 600 °C for 2 h. The activated sample was exposed to 0.67 kPa of methanol at room temperature, and then evacuated at the same temperature for 5 min. IR spectra were recorded at room temperature by using a JASCO FT/IR 4200 spectrometer at a resolution of 4 cm⁻¹.

2.3. Catalytic activity measurement

The catalytic activity for oxidative coupling of methane and NO decomposition reactions was evaluated using a fixed-bed continuous flow reactor.

(A) *Oxidative coupling of methane (OCM)*: The reaction gas composed of 44.4% CH₄ and 11.1% O₂ diluted with He as the balance gas was fed to a 0.1 g catalyst that had been pretreated *in situ* in a flow of He at 650 °C for 2 h at a rate of 45 cm³ min⁻¹. The reaction temperature was increased from 650 to 750 °C in steps of 50 °C, and the steady-state catalytic activity was measured at each temperature.

(B) *NO decomposition*: The reaction gas composed of 1% NO with He as the balance gas was fed to a 0.1 g catalyst that had been pretreated *in situ* in a flow of He at 600 °C for 2 h at a rate of 50 cm³ min⁻¹.

Table 1
Crystallite size and BET surface area of Y_2O_3 .

	Preparation method	Crystallite size ^a (nm)	BET surface area (m ² g ⁻¹)	Calculated surface area ^b (m ² g ⁻¹)
$Y_2O_3(P)$	Precipitation using NH_3	10.6	76.7	93.8
$Y_2O_3(RP)$	Reverse precipitation using NH_3	13.5	51.4	73.6
$Y_2O_3(HP)$	Homogeneous precipitation using urea	13.4	18.7	74.2
$Y_2O_3(HT)$	Hydrothermal at 200 °C	6.04	61.6	164.6

^a The crystallite size of Y_2O_3 was calculated from the XRD peak, given in Fig. 1, from the (222) plane using Scherrer's equation.

^b Surface area was calculated from the crystallite size using the following equation, $S = 5/(\rho \cdot d)$, where ρ is a density of Y_2O_3 (5.03 g cm⁻³) and d is the crystallite size, by assuming spherical particles.

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