Characteristics of methane combustion over La–Cr–O catalysts

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The catalytic activities of methane combustion of La–Cr–O catalysts prepared with and without polyacrylic acid as a template have been compared. The polymer-templated catalyst had a higher BET surface area, 12.3 $m^2\,g^{-1}$, than that obtained from the conventional precipitation method, 2.9 $m^2\,g^{-1}$. The results of XRD and SEM experiments suggested that the structural characteristics were almost similar. Surprisingly, the areal rate of methane combustion over the catalyst with a small surface area was ten times larger than that of the catalyst with a large surface area. However, the site time yields (STY) based on the oxygen adsorption capacity were similar, independent of the surface area and preparation conditions.

Keywords: La–Cr–O catalyst, methane, combustion, oxygen adsorption

1. Introduction

Catalytic combustion is an environmentally benign process without pollutant emissions. Typically, NO_x emission can be reduced dramatically to a few ppms, since the combustion temperature can be maintained below 1673 K [1,2]. Thus, the catalytic combustion technology has been considered as one of the promising technologies for reducing hazardous exhaust gases emissions. Therefore, detailed characteristics of the combustion on catalytic surfaces are worthy of investigating for the better design of catalytic material.

In general, it is believed that the catalytic activity in combustion is proportional to the surface area and the amount of incorporated active components. Thereby, much effort has been directed to finding thermally stable catalytic material at high temperature. Hexaaluminates pioneered by Arai’s group at Kyushu University are among them [3]. Klvana et al. showed that the catalytic activity of methane combustion was proportional to the surface area of perovskites prepared using a freeze-drying method [4]. The results indicated that the combustion activity increased with the surface area up to 10 $m^2\,g^{-1}$. Indeed, the preparation method can affect the catalytic performance.

However, information on catalytically active centers dispersed on metal oxides has been very limited to clarify the relationship among the combustion activity, surface area and catalytic site. In the present work, we have made model La–Cr–O catalysts using a polymer template in order to compare the catalytic performance. The catalysts were characterized with XRD, N_2 BET method, oxygen adsorption, TGA and scanning electron microscopy. The obtained catalytic performance of the catalysts was analyzed based on the above characterization results.

2. Experimental

Polyacrylic acid (45%, M.W. = 5,000, Aldrich) was used as a template. $La(NO_3)_3{\cdot}6H_2O$ (99%, Aldrich) and $Cr(NO_3)_3{\cdot}9H_2O$ (99%, Aldrich) were used as metal precursors. The polyacrylic acid solution was diluted with deionized water (50 : 50 vol%). Each metal salt was dissolved in deionized water. The salt solution was added dropwise while stirring vigorously at room temperature. First, La solution was added and subsequently Cr solution was added. The color of the mixture turned to darkish green. The composition was $La^{3+} : 2Cr^{3+} : 3\text{–}6RCOOH$, where RCOOH represents functional group of the polymer chain. Gellation started with stirring upon addition of concentrated aqueous ammonia solution. The pH of the mixture was increased from 1 to 7–8 upon neutralization. The gel was aged in an oven at 373 K overnight.

The as-precipitated product was filtered, washed three times with deionized water and subsequently dried in an oven at 373 K. The obtained product was calcined in air while temperature increased up to 1073 K with a rate of 1 $K\,min^{-1}$. For a comparison, a sample of the same composition was synthesized in the same way without the polymer template.

Oxygen adsorption was measured volumetrically at 298 K after the evacuation of the sample at 673 K until 1.0×10^{-3} Pa. Thermogravimetric analysis of the product was performed using a TGA2050 (TA Instrument). X-ray powder diffraction patterns of the calcined sample were recorded in the range of $2\theta = 10\text{–}80^\circ$ using either a Rigaku D/MAX (III) or a Rigaku Miniflex with Cu K_α source. The scan speed was $4^\circ\,min^{-1}$. BET surface areas were measured at liquid-nitrogen temperature using a Micromeritics ASAP2000 instrument. SEM micrographs were taken using a Philips XL-30 instrument with an accelerating voltage of 10 kV after pasting the calcined powder to 3M tape.

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Catalytic combustion of methane was performed using a fixed-bed flow reactor in a temperature range of 373–973 K. The reactant gas consisted of 1 vol% methane and 99 vol% air. The effluent gases were analyzed by a gas chromatograph (HP5890, Hewlett Packard) equipped with TCD and FID detectors.

3. Results and discussion

The polymer template used in the synthesis can be removed by heating in air at 1073 K. Thermogravimetric analysis indicated that the polymer template started to decompose at 500 K, as shown in figure 1, while the La and Cr salts decomposed below 500 K. Two significant weight changes were observed at 710 and 880 K, respectively, which were believed to be due to the formation of a perovskite phase [5]. The results of thermogravimetric analysis indicated that the temperature in calcination of the as-precipitated product should increase up to 1000 K in order to remove the polymer.

XRD diffraction patterns of the La–Cr–O catalysts are shown in figure 2. The as-precipitated product did not give any distinguished peak corresponding to metal oxide or polyacrylic acid. The analysis of XRD patterns of the calcined La–Cr–O catalysts at 1073 K showed the presence of $Cr_{1.01}LaO_{3\pm\delta}$ and $LaCrO_3$ phases. The catalyst synthesized in the presence of the polymer template contained 76% $Cr_{1.01}LaO_{3\pm\delta}$, 7% Cr_2O_3, and 15% $LaCrO_3$. The comparative sample synthesized without the polymer template had the similar phase composition. It was reported that $Cr_{1.01}LaO_{3\pm\delta}$ can be prepared from La_2O_3 and $Cr(NO_3)_3{\cdot}9H_2O$ by the glycine-nitrate method [6].

SEM micrographs of the La–Cr–O catalysts are presented in figure 3. The estimated particle size was ~0.2 μm. The catalyst synthesized in the presence of the polymer template had more or less small particles, indicating the increase of surface area compared to the precipitated catalyst in the absence of the polymer template. It was of note that the particle shape of the catalyst synthesized using the polymer template was rather sharp compared to the more spherical particles in the precipitated catalyst. The specific surface areas of these two catalysts measured at 77 K were 12.3 and 2.9 $m^2\ g^{-1}$, respectively.

Catalytic activity of the methane combustion is plotted as a function of temperature in figure 4. Reaction rates expressed in unit surface area at 873 K are listed in table 1.

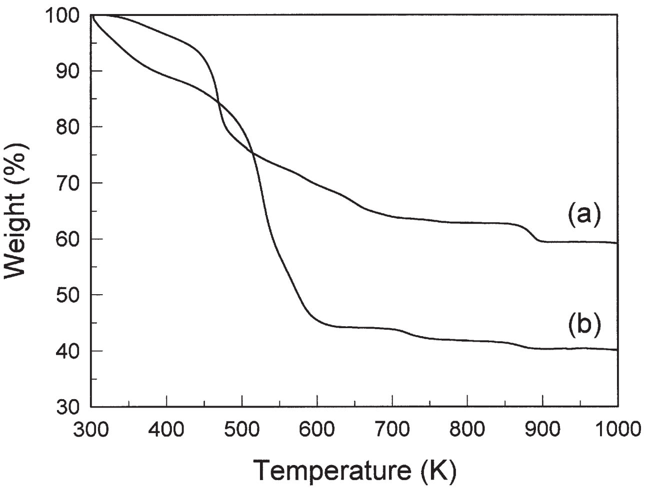

Figure 1. TGA patterns of (a) La–Cr–O catalyst synthesized in the presence of polymer and (b) precipitated La–Cr–O catalyst without polymer.

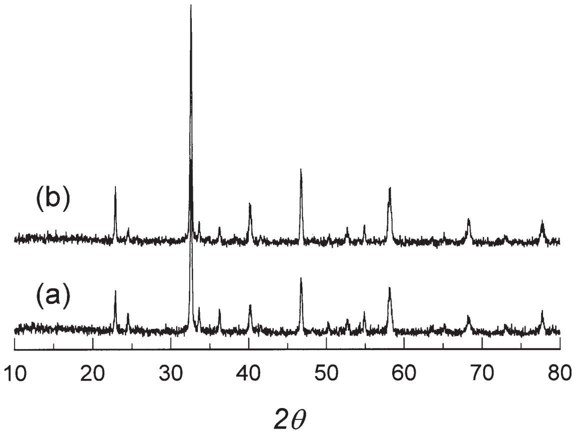

Figure 2. XRD patterns of (a) La–Cr–O catalyst synthesized in the presence of polymer and (b) precipitated La–Cr–O catalyst without polymer. The catalysts were calcined in air at 1073 K for 6 h.

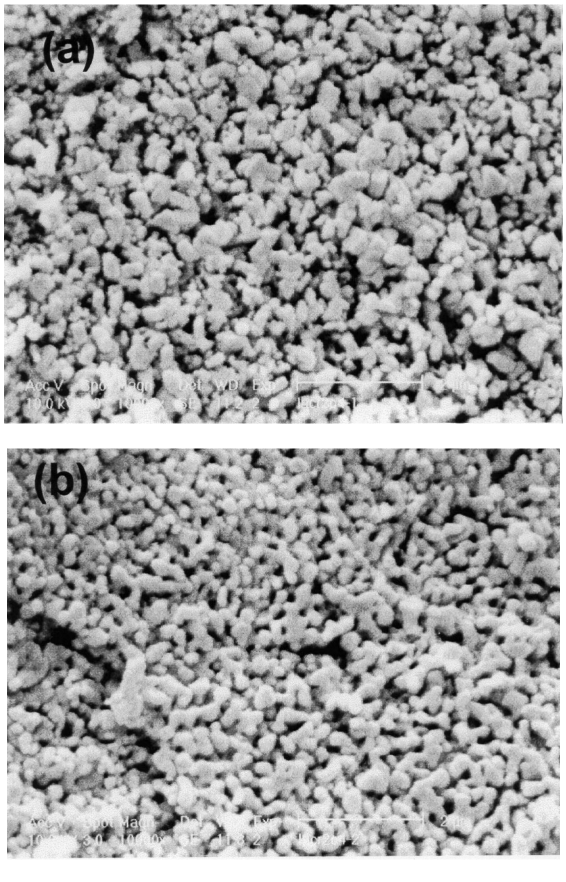

Figure 3. SEM micrographs of (a) La–Cr–O catalyst synthesized in the presence of polymer and (b) precipitated La–Cr–O catalyst without polymer.

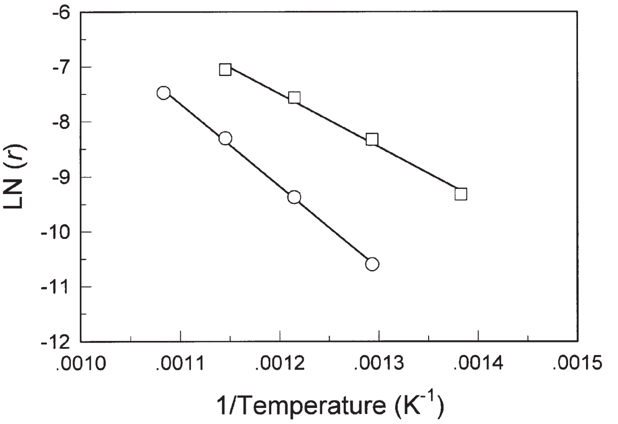

Figure 4. Arrhenius plot of methane combustion over (○) La–Cr–O catalyst synthesized in the presence of polymer and (□) precipitated La–Cr–O catalyst without polymer.

Table 1
Result of N_2 BET surface area measurement and methane combustion over the La–Cr–O catalysts.

Template	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	r^{a} ($\mu\mathrm{mol\,s^{-1}\,m^{-2}}$)	E_{a} ($\mathrm{kJ\,mol^{-1}}$)	STY^{b} ($\mathrm{s^{-1}}$)
Yes	12.3	0.06	124.2	3.0
No	2.9	0.96	80.0	2.1

[a] Areal rate at 873 K.

[b] Site time yield of methane conversion based on amount of oxygen adsorption at 20 kPa that was equal to oxygen content in air approximately.

The areal rate of the La–Cr–O catalyst synthesized in the presence of the polymer template was much smaller than that of the small surface area catalyst. Different activation energies for both catalysts were also obtained.

It has been reported that the activity of total oxidation of hydrocarbons over perovskite catalysts is related with a defective structure such as oxygen vacancy [7]. Partial substitution at A sites may enhance further the catalytic performance [8]. However, the nature of adsorbed oxygen is not uncovered clearly. The observed kinetics of hydrocarbon oxidation over the perovskite catalyst can be accounted for considering the two oxygen species, the adsorbed α-oxygen and the lattice oxygen [9]. The La–Cr–O catalyst prepared in the present work contained the perovskite structures $\mathrm{Cr_{1.01}LaO_{3\pm\delta}}$ and $\mathrm{LaCrO_3}$. Thus, it was believed that the observed catalytic activity can be related to the oxygen-defective or -deficient sites. The amount of oxygen adsorption sites may be proportional to the oxygen-defective or -deficient sites, since the perovskite has been reported to adsorb and desorb oxygen on cooling in oxygen and heating *in vacuo*, respectively [7].

In order to clarify the relationship between the surface area and the present combustion activity data, oxygen adsorption was measured over both catalysts. Figure 5 shows oxygen adsorption isotherms on the La–Cr–O catalysts at 298 K. The amount of oxygen adsorption was much smaller for the La–Cr–O catalyst synthesized in the presence of the polymer template, compared to that of the precipitated La–Cr–O catalyst without the polymer.

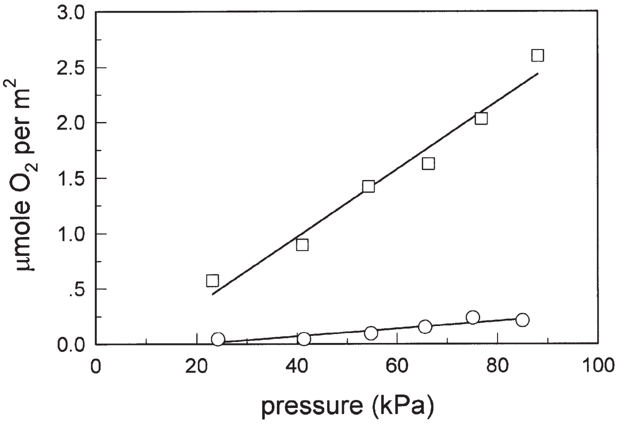

Figure 5. Oxygen adsorption isotherms on (○) La–Cr–O catalyst synthesized in the presence of polymer and (□) precipitated La–Cr–O catalyst without polymer, at 298 K.

Catalytic activity can be expressed according to various definitions: gram activity, areal rate, turnover rate, site time yield [10], space time yield, etc. Among them, the exact measurement of turnover rate can be very useful to compare the rate data from different laboratories, to deal with the occurrence of poisoning, to investigate new catalytic materials and to find the role of promoter or additive [11]. More safely, site time yield (STY) defined as the number of a specified product made per catalytic site and per unit time was preferred in the present work.

The same reactivities of both catalysts, STYs, were obtained within error range based on the amount of oxygen adsorption. Therefore, it was reasonable to assume that the catalytic sites for methane combustion were the same in nature, independent of preparation method or surface area. Similarly, the same nature of Pt catalyst supported on KL zeolite before and after sulfur poisoning was suggested from the measurement of turnover rate of n-hexane aromatization [12].

In the present work, we assumed that the oxygen-deficient site was a catalytic site. However, lattice oxygen can contribute to the catalytic performance at high temperature above 1073 K. Few oxygen-deficient sites in the La–Cr–O catalyst synthesized in the presence of polymer were believed to originate from the much more perfect formation of micro crystals in the polymer template, compared to the formation of metal oxide without the polymer. However, more surface characterization is necessary to clarify this point.

In summary, the STY of the La–Cr–O catalyst was the same independent of the surface area and the preparation conditions, indicating the catalytic site was the same in nature.

References

[1] D.L. Trimm, Catal. Today 26 (1995) 231.
[2] M.F.M. Zwinkels, S.G. Jaras and P.B. Menon, Catal. Rev. Sci. Eng. 35 (1993) 319.
[3] H. Arai and M. Machida, Appl. Catal. A 138 (1996) 161.

[4] D. Klvana, J. Kirchnerova, J. Chaouki and P. Gauthier, in: *Proceedings of International Workshop on Catalytic Combustion*, 18–20 April 1994, ed. H. Arai (Catalysis Society of Japan, Tokyo, 1994) p. 24.
[5] H.M. Zhang, Y. Shimizu, Y. Teraoka, N. Miura and N. Yamazoe, J. Catal. 121 (1990) 432.
[6] JCPDS Card No. 44-0333.
[7] T. Seiyama, in: *Properties and Applications of Perovskite-Type Oxide*, eds. L.G. Tejuca and J.L.G. Fierro (Dekker, New York, 1993) ch. 10.
[8] T. Seiyama, N. Yamazoe and K. Eguchi, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 19.
[9] T. Nakamura, N. Misono and Y. Yoneda, Chem. Lett. (1981) 1589.
[10] M. Boudart, Catal. Rev. Sci. Eng. 23 (1981) 1.
[11] M. Boudart, Chem. Rev. 95 (1995) 661.
[12] G.B. McVicker, J.L. Kao, J.J. Zeimiak, W.E. Gates, J.L. Robbins, M.M.J. Treacy, S.B. Rice, T.H. Vanderspurt, V.R. Cross and A.K. Ghosh, J. Catal. 139 (1993) 48.