[Regular Paper]

Effects of Additives on SrO-La₂O₃ Catalysts for Oxidative Coupling of MethaneKiyomi OKABE*, Kazuhiro SAYAMA, Hitoshi KUSAMA,
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Oxidative coupling of methane was carried out over MO_x-SrO/La₂O₃ catalysts (MO_x is an additive and M: Sr: La=1:1:10) in a flow of CH₄-O₂ mixture (CH₄/O₂=10) and in the temperature range of 1,023–1,123 K. The surface basicity of the catalysts evaluated by CO₂-TPD, increased by the addition of alkali and alkaline earth metal oxides. The surface basicity was correlated with the binding energy difference between XPS La 3d and O 1s levels of the catalyst. A good correlation between surface basicity and C₂+ selectivity was obtained at reaction temperature *T*=1,023 K. However, the correlation was unclear at higher temperatures. Different correlations were explained in terms of the difference in the desorption rate of the intermediate depending on the reaction temperature.

1. Introduction

Among the various kinds of catalysts for oxidative coupling of methane, SrO/La₂O₃ has so far been recognized as being one of the most promising ones for selective production of C₂+ hydrocarbons^{1)–3)}. In a previous paper⁴⁾, the effect of catalyst preparation on oxidative coupling of methane over SrO-La₂O₃ catalysts has been reported. The effect of catalyst preparation on surface morphology and basicity of the catalysts, and high selectivity to C₂+ hydrocarbons were obtained using columnar-shaped catalysts. However, the effect of basicity on the reaction is still controversial for other types of catalysts. Although it is generally accepted that conversion is proportional to the number of surface basic sites^{5)–7)}, the dependency of C₂+ selectivity on the surface basicity of the catalysts is not yet clear. Over some catalysts, such as molten alkali metal carbonates⁸⁾, alkaline earth metal salts^{9)–11)}, rare earth metal salts^{11),12)}, and alkali metal doped catalysts^{13)–15)}, C₂+ selectivity is reported to be directly proportional to basicity; however there is no correlation between catalytic and basic properties for the others, such as MgO¹⁶⁾, supported alkali and alkaline earth metal catalysts^{17),18)}, and ZnO-TiO₂ catalysts¹⁹⁾. Over some catalysts, such as BaO-CaO²⁰⁾, it is claimed that basic sites with

certain base strengths are responsible for C₂+ selectivity. It is also asserted that the combination of basic and acidic sites is important for the selectivity over La₂O₃ catalysts²¹⁾. Moreover, even the same authors may draw inconsistent results on the dependency of C₂+ selectivity on the surface basicity of different kinds of catalysts. It may be considered that different reaction conditions and different means of comparison give ambiguous results on the dependency of selectivity on catalyst basicity. In order to remove this ambiguity, the effect of surface basicity on selectivity should be elucidated by comparing the catalytic performances made over a series of similar catalysts under the same conditions. For this purpose, various metal oxides were added to SrO-La₂O₃ catalysts to provide a wide range of basicity, and the oxidative coupling of methane was carried out under the same conditions.

2. Experimental

A columnar-shaped La₂O₃ catalyst was prepared from LaCl₃·7H₂O by coprecipitation with urea as described previously⁴⁾. It was then impregnated with aqueous solutions of Sr(NO₃)₂ and various metal (M) nitrates or chlorides to form various types of MO_x-SrO/La₂O₃ catalysts (M: Sr: La=1:1:10 in atomic ratio). After calcination at 1,173 K, 0.3 g of catalyst was packed in a fixed-bed reactor and used for oxidative coupling of methane

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Fig. 1 SEM Images of (a) La_2O_3 , (b) $\text{Li}_2\text{O-SrO/La}_2\text{O}_3$, and (c) $\text{CaO-SrO/La}_2\text{O}_3$ Catalysts Calcined at 873 K

in a flow of $\text{CH}_4\text{-O}_2$ mixture ($\text{CH}_4/\text{O}_2=10$) at a rate of $440\text{ cm}^3/\text{min}$ and in the temperature range of 1,023-1,123 K. The reaction products were analyzed by the on-line gas-chromatography, at the end of 1 h reaction at each temperature. The surface basicity of the catalysts was evaluated by $\text{CO}_2\text{-TPD}$ heating up to 1,200 K at a rate of 10 K/min in a flow of He at a rate of $30\text{ cm}^3/\text{min}$. The desorption of pre-adsorbed CO_2 from the calcined catalysts was detected by using a mass spectrometer.

Bulk concentrations of the additives in the catalysts were determined by an X-ray fluorescence spectrometer (Seiko SEA 2010).

X-Ray photoelectron spectra of catalysts were recorded with Shimadzu ESCA-850 without exposure to open-air after pretreatment at 773 K in a flow of dry air at $100\text{ cm}^3/\text{min}$ within the pre-chamber of the apparatus. The binding energies of XPS were referred to the evaporated Au on the surface as the internal standard with Au $4f_{7/2}$ level at 83.8 eV.

3. Results and Discussion

The results of bulk and surface analyses of $\text{MO}_x\text{-SrO/La}_2\text{O}_3$ catalysts are listed in Table 1. The surface concentrations of Sr were almost identical ($\text{Sr/La}=0.2$), regardless of the bulk concentrations, as pointed out previously⁴. As for other additives (MO_x), the surface concentrations of alkali metals were much higher than those of the bulk ones, indicating that the surfaces were highly covered with alkali metal additives. The surface morphology of the alkali-metal-added catalysts was different from that of the original La_2O_3 catalyst (*i.e.*, La_2O_3 without any additive), and it was almost the same irrespective of the kind of alkali metals added. The SEM images of alkali-

Table 1 Bulk^{a)} and Surface^{b)} Analyses of $\text{MO}_x\text{-SrO/La}_2\text{O}_3$ Catalysts ($\text{MO}_x=\text{additive}$)

Additive MO_x	Sr/La		M/La	
	Bulk	Surface	Bulk	Surface
Na_2O	0.1	0.2	* ^{c)}	0.5
K_2O	0.1	0.3	0.1	0.6
Cs_2O	0.1	0.2	0.1	0.5
MgO	0.1	0.2	* ^{c)}	0.1
CaO	0.1	0.2	0.1	0.1
SrO	0.2	0.3	—	—
ScCl_3	0.1	0.2	0.1	0.1
YCl_3	0.1	0.2	0.1	0.1
TiCl_3	0.1	0.2	* ^{d)}	0.1
ZrO_2	0.1	0.2	0.1	0.1

a) Determined by X-ray fluorescence analysis (XRF).

b) Determined by XPS.

c) Less than detection limit.

d) Could not be determined by XRF.

metal-added catalysts are represented by $\text{Li}_2\text{O-SrO/La}_2\text{O}_3$, as shown in Fig. 1. In contrast, the surface concentrations of alkaline earth metals and others were almost the same as those of the bulk ones, and the surface morphology was similar to the original La_2O_3 suggesting a homogeneous distribution of these additives. The SEM images of alkaline-earth-metal-added catalysts are represented by $\text{CaO-SrO/La}_2\text{O}_3$ in Fig. 1.

The surface basicity of calcined catalysts was evaluated at maximum temperature (T_M) in the $\text{CO}_2\text{-TPD}$ spectra illustrated in Fig. 2. The T_M was higher than 1,100 K when alkali or alkaline earth metal oxides were added. The T_M decreased to a range of 800-1,000 K when chlorides were used as additives, but the T_M still remained higher than that of the original La_2O_3 catalyst.

The XPS O 1s levels showed two peaks at about 532 and 529 eV. The former was assigned to the oxygen of the adsorbed species, and the latter to the lattice oxygen²². In order to minimize the charge-up effect, the values of binding energy differences (ΔE_b) between the latter and La 3d

Fig. 2 CO₂-TPD Spectra of (a) Na₂O-SrO/La₂O₃, (b) MgO-SrO/La₂O₃, (c) ZrO₂-SrO/La₂O₃, (d) YCl₃-SrO/La₂O₃, (e) CaCl₂-SrO/La₂O₃, and (f) La₂O₃ Catalysts

levels, instead of the absolute values, were used to characterize the electronic states of the levels. The ΔE_b varied with the additives involved. The binding energy difference qualitatively reflects the charge distribution between the La-O bonds. A large difference implies that La is more positively and/or O is more negatively charged, and that the La-O bond has more ionic (*i.e.*, less covalent) properties. By taking into consideration that alkaline metal oxides are more ionic than transition metal oxides, the binding energy shifts qualitatively correlate with the alkalinity of metal M' in the M'-O bond. A correlation between T_M in Fig. 2 and ΔE_b was obtained, as shown in Fig. 3, implying that ΔE_b can be used as an indicator for surface basicity of the catalysts.

Results of reaction at $T=1,023$, $1,073$ and $1,123$ K, and surface areas of the catalysts are listed in Table 2. The surface areas decreased by addition of alkali metal oxides, but they did not decrease by addition of most of the other additives. The changes in the surface morphology by alkali metal additives may be responsible for the decrease in the surface areas. At reaction temperature $T=1,023$ K, both CH₄ and O₂ conversions tended to be low when the surface area was small. Relatively low conversions over the catalysts containing alkali metal oxides may be ascribed to the small surface areas, as well as to the strong basicity evaluated by T_M in Fig. 2. As has been pointed out elsewhere²³⁾, the catalysts that are too

Characters denote additives.

Fig. 3 Correlation between Maximum Temperature (T_M) in Fig. 2 and Binding Energy Difference (ΔE_b) between La 3d and O 1s Levels of Lattice Oxygen of XPS

basic may be inactive at low reaction temperatures, because the active sites are easily covered with CO₂, a by-product, under these reaction conditions.

The selectivity to C₂⁺ hydrocarbons increased, except for TiCl₃, depending on the additives at $T=1,023$ K. A good correlation between selectivity and T_M in Fig. 2 was obtained, as depicted in Fig. 4. The correlation strongly suggests that the catalysts with strong basicity are favorable for higher selectivity. In contrast, the correlation was unclear at temperature as high as $T=1,123$ K as shown in Fig. 5. The difference in dependency of selectivity on the surface basicity may be explained in terms of the difference in relative reaction rates at elementary steps of the reaction. The reaction scheme is generally described as follows (see Scheme 1): The reaction proceeds *via* CH₃ radical formation. The CH₃ radicals dimerize into C₂ hydrocarbons in the gas phase, whereas the radicals reacting with the adsorbed oxygen species on the surface are converted into oxygen-containing surface species, which are believed to be the intermediate for deep oxidation^{24)~34)}. If the desorption of CH₃ radicals from the surface (1) is

Scheme 1 Reaction Scheme of Oxidative Coupling of Methane

Characters denote additives.

Fig. 4 Correlation between C₂+ Selectivity at T=1,023 K and Maximum Temperature (T_M) in Fig. 2

Characters denote additives.

Fig. 5 Correlation between C₂+ Selectivity at T=1,123 K and Maximum Temperature (T_M) in Fig. 2

Table 2 Results of Methane Oxidative Coupling over MO_x-SrO/La₂O₃ Catalysts (MO_x=additive; M/Sr/La=1/1/10)

Catalyst	Surface area (S) [m ² ·g ⁻¹]	Reaction temp. (T) [K]	CH ₄ conv. [%]	O ₂ conv. [%]	C ₂ + selec. [%]
La ₂ O ₃	4.1	1,023	9.2	71.4	55.6
		1,073	11.9	87.5	67.9
		1,123	13.1	96.7	69.2
Li ₂ O-SrO/La ₂ O ₃	1.9	1,023	5.1	38.0	76.7
		1,073	10.8	73.8	80.5
		1,123	12.9	89.2	79.0
Na ₂ O-SrO/La ₂ O ₃	2.6	1,023	8.2	54.2	81.8
		1,073	13.2	85.5	80.9
		1,123	13.8	94.8	77.7
Cs ₂ O-SrO/La ₂ O ₃	2.3	1,023	10.8	66.5	74.5
		1,073	12.1	76.0	74.5
		1,123	12.6	83.5	72.0
MgO-SrO/La ₂ O ₃	10.6	1,023	12.7	89.4	76.4
		1,073	14.1	94.3	79.5
		1,123	14.3	96.1	80.2
CaO-SrO/La ₂ O ₃	6.7	1,023	13.9	93.4	79.6
		1,073	15.0	97.0	82.0
		1,123	14.8	98.0	80.8
SrO/La ₂ O ₃	12.1	1,023	12.7	95.2	72.4
		1,073	13.4	98.8	76.2
		1,123	13.4	100.0	76.2
MgCl ₂ -SrO/La ₂ O ₃	4.9	1,023	7.8	64.7	65.0
		1,073	9.4	73.6	74.3
		1,123	10.4	87.7	71.4
CaCl ₂ -SrO/La ₂ O ₃	2.9	1,023	7.9	61.4	66.9
		1,073	9.5	69.5	76.6
		1,123	10.5	80.9	75.3
ScCl ₃ -SrO/La ₂ O ₃	6.8	1,023	11.4	83.1	67.9
		1,073	13.8	93.2	77.4
		1,123	14.4	98.2	78.7
YCl ₃ -SrO/La ₂ O ₃	3.1	1,023	11.4	78.9	67.3
		1,073	14.7	92.2	78.4
		1,123	15.2	97.5	79.2
TiCl ₃ -SrO/La ₂ O ₃	14.3	1,023	7.7	69.9	53.9
		1,073	9.1	73.1	68.6
		1,123	12.0	89.4	78.2
ZrO ₂ -SrO/La ₂ O ₃	9.6	1,023	14.6	91.5	72.0
		1,073	15.1	96.8	77.0
		1,123	15.9	99.3	74.8

sufficiently slow compared to the surface reaction (2), selectivity depends on the surface reactivity of the intermediate, which may reflect surface basicity. However, if the desorption is sufficiently fast, which is often the case at high temperatures, the secondary reaction on the surface may not be important, resulting in similar selectivity, and the selectivity does not reflect the surface properties of the catalyst.

In conclusion, the correlation between C₂⁺ selectivity and basicity of the catalysts depended on reaction temperature. The dependency was explained in terms of the relative reaction rates at elementary steps. As a consequence, the highest C₂⁺ hydrocarbons yield of 12.3 % (CH₄ conv.=15.0 % and C₂⁺ selec.=82.0%) was obtained over CaO–SrO/La₂O₃ catalyst at 1,073 K. The results of XPS may be used as an indicator for basicity on the surface of the catalyst.

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要 旨

メタン酸化カップリング反応における SrO-La₂O₃ 触媒への添加物の効果

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メタン-酸素混合ガス (CH₄/O₂=10) を用い, 含浸法で調製した MO_x-SrO/La₂O₃ 系触媒 (MO_x は添加物, M: Sr: La=1: 1: 10) 上でのメタン酸化カップリング反応を 1,023 ~ 1,123 K の温度範囲において行った。CO₂-TPD によって評価される触媒表面の塩基強度は, アルカリおよびアルカリ土類金属酸化物の添加により増大した。一方, 触媒の XPS を測定したところ, La 3d と O 1s 軌道準位の結合エネルギー差と触媒の塩基強度との間には相関が認められ, この XPS 結合エネルギー差 (ΔE_b) は触媒表面の塩基性質の指標になり得ることが

示された。反応温度 1,023 K においては触媒の塩基強度と C₂₊ 選択率との間により相関が認められたが, 高温においては相関性は不明確だった。このような触媒の塩基性と選択率との間の相関性の反応温度依存性は, 高温では触媒表面からの反応中間体の脱離が支配的になるため, 表面二次反応の重要性が相対的に低下し, 触媒の塩基性質が反応結果に反映され難くなるためと説明された。結果的に, CaO-SrO/La₂O₃ 触媒において反応温度 1,073 K で最高 12.3% の C₂₊ 収率が得られた。

Keywords

Additive, Basicity, Lanthanum oxide catalyst, Methane, Oxidative coupling, XPS