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Effect of Catalyst Preparation on the Oxidative Coupling of Methane over SrO–La_2O_3

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(Received February 28, 1994)

Synopsis. The surface Sr/La ratio of SrO–La_2O_3 catalysts was almost unchanged within the bulk ratio of Sr/La= 0.02—0.2 when calcined at 1173 K. The reaction results showed that the selectivity to C_{2+} hydrocarbons depends on the catalyst preparation, which affects the surface morphology and the basicity of the catalysts.

Various kinds of catalysts have been proposed for oxidative coupling of methane since the pioneering work reported by Keller and Bhasin.[1)] Among them, SrO/La_2O_3 has been recognized as being one of the most promising catalysts for the selective production of C_{2+} hydrocarbons so far.[2—4)] Relatively little attention has been paid, however, from a morphological point of view on SrO/La_2O_3 catalysts.[5—9)] In a previous paper,[10)] we prepared various La_2O_3 catalysts by different methods, and reported the effects of the surface morphology on the reaction. In order to improve the selectivity further, morphologically different La_2O_3 catalysts were modified with SrO, and the effect of preparation and/or pretreatment conditions on the reaction was discussed.

Experimental

Various SrO–La_2O_3 catalysts (Sr/La=0.0—0.2) were prepared from nitrates by co-precipitation with urea, a hydrothermal reaction, co-precipitation with Na_2CO_3, spray pyrolysis, and impregnation, as described previously,[10)] and denoted as Catalyst A, B, C, D, E, respectively. After calcination at a temperature range of 873—1773 K for 4 h, 0.3 g of the catalyst was packed in a fixed-bed reactor, and used for the oxidative coupling of methane in a CH_4–O_2 mixed flow ($CH_4/O_2=10$) at a flow rate of 440 $cm^3\,min^{-1}$ and a temperature range of 973—1123 K. The reaction products were analyzed by on-line gas-chromatography.

Results and Discussion

Figure 1 shows SEM images of catalysts (Sr/La=0.2) calcined at 873 K. The crystal shapes were columnar with smooth and rough surfaces, flaky, and spherical, for Catalyst A, B, C, and D, respectively. By calcination at 1173 K, the crystals were sintered, but still partially had the original characteristics of shape.

The XRD patterns of catalysts indicated that the main phases could be identified as $La_2O_2CO_3$ (or La_2CO_5) and La_2O_3 by calcination at 873 and 1173 K, respectively, regardless of any difference in the surface morphology. None of the SrO–La_2O_3 double-oxide phases reported in the literature[11)] were detected in the XRD patterns, implying a high dispersion of the Sr-component. The XPS results indicated that the surface Sr/La ratio of calcined catalysts was not significantly varied within the bulk ratio of Sr/La=0.02—0.2, as listed in Table 1. This result suggests that a certain phase with a specific Sr/La ratio is formed on the surface by calcination. A trace amount of Na (Na/La< 0.01) was detected on the surface of Catalyst C.

The TGA profiles (in differential forms) of as-prepared catalyst are depicted in Fig. 2. The peaks at about 610 and 760 K were identified by mass spectrometry as desorption of H_2O and H_2O+CO_2, and the others as CO_2 from the catalysts by thermal decomposition. Upon the addition of SrO to La_2O_3 (Sr/La=0.2), an additional peak was observed at about 1140 K, besides peaks of the La-component. The position of the additional peak was different from that of $SrCO_3$, itself, suggesting that a new phase was formed in the catalyst by an interaction between La and Sr.

The basicity of the calcined catalysts was evaluated by CO_2-TPD at a heating rate of 10 $K\,min^{-1}$, as illustrated in Fig. 3. The desorption of pre-adsorbed CO_2 from the catalysts was detected by using a mass spectrometer. The solid and broken lines denote the desorption from catalysts calcined at 1173 and 1773 K, respectively. Except for Catalyst C (e), the peak maximum temperature (T_M) jumped up from approximately T_M=690 K to T_M=1055—1080 K discontinuously upon adding SrO to La_2O_3, irrespective of the Sr-content from Sr/La=0.05 to 0.2 when the catalysts were cal-

Table 1. Bulk and Surface Sr/La Ratios of SrO–La_2O_3 Catalysts

Catalyst	Bulk Sr/La[a)]	Surface Sr/La[b)]	
		Calcined at 873 K	Calcined at 1173 K
Catalyst A	0.17	0.27	0.25
	0.10	0.21	0.24
	0.02	0.16	0.18
Catalyst B	0.23	0.19	0.24
Catalyst C	0.25	0.14	0.17
Catalyst E	0.19	0.24	0.21
	0.11	0.20	0.22
	0.05	0.15	0.23
	0.02	0.16	0.22

a) Determined by X-ray fluorescence analysis. b) Determined by XPS.

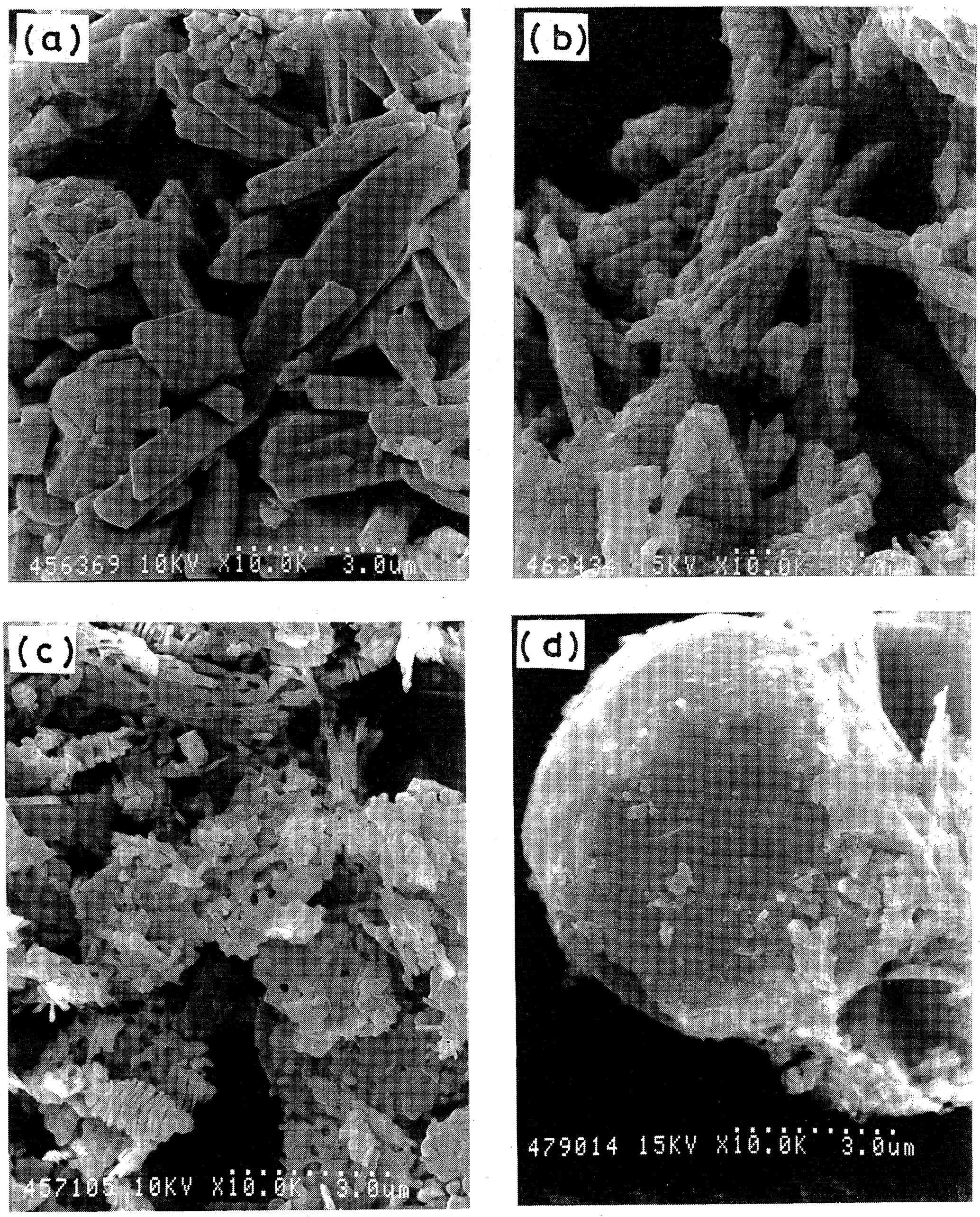


Fig. 1. SEM Images of SrO–La_2O_3 catalysts calcined at 873 K. (a) Catalyst A, (b) Catalyst B, (c) Catalyst C, and (d) Catalyst D.

cined at 1173 K. The jump in T_M indicates that the strength of the basicity increases discontinuously upon the addition of SrO. The T_M was, however, much lower than that of $SrCO_3$, implying a weaker basicity than that of $SrCO_3$.

By calcination at 1773 K, the TPD peak areas decreased drastically, and the positions shifted to a lower temperature side, implying that both the strength and quantity of the basicity decrease due to calcination. The change in the basicity due to calcination is also supported by a decrease in the O 1s XPS peak areas of the adsorbed oxygen species and surface areas.

The reaction results at reaction temperatures of $T=973$ K and $T=1123$ K are listed in Table 2. Generally, high selectivity to C_{2+} hydrocarbons was obtained over catalysts calcined at 1173 K. By calcination at a higher temperature, both CH_4 conversion and C_{2+} selectivity decreased, indicating that the amount and strength of the basicity decreased remarkably.

At a reaction temperature of $T=973$ K, both CH_4 conversion and C_{2+} selectivity were varied by the preparation method (or surface morphology). Higher selectivity tended to be obtained over catalysts with a higher T_M in the CO_2-TPD spectra, except for Cata-

Table 2. Reaction Results over $SrO–La_2O_3$ Catalysts (Sr/La=0.2)

Catalyst	Calcination temperature	Surface area	T=973 K CH$_4$ conv.	T=973 K O$_2$ conv.	T=973 K C$_{2+}$ selec.	T=1123 K CH$_4$ conv.	T=1123 K O$_2$ conv.	T=1123 K C$_{2+}$ selec.
	T_c/K	m^2 g^{-1}	%	%	%	%	%	%
Catalyst A	873	4.0	6.3	57.6	43.5			
	1173	0.9	8.1	62.2	52.3	14.2	93.7	75.6
	1773	<0.1	1.6	13.5	35.4	11.0	75.9	73.6
Catalyst B	873	4.7	7.4	63.9	54.5			
	1173	<0.1	8.4	69.8	61.0	13.8	95.7	76.4
	1773	<0.1	1.2	5.6	23.6	5.2	37.5	62.6
Catalyst C	873	2.8	4.3	40.8	29.1			
	1173	1.4	3.6	32.1	38.9	13.2	99.7	76.2
	1773	<0.1	1.7	13.3	39.7	8.5	60.3	72.1
Catalyst D	1273	7.1	7.3	74.5	42.8	11.8	99.6	68.3
Catalyst E	873	13.9	9.0	77.1	54.9			
	1173	5.0	10.4	79.2	57.9	14.5	98.6	74.0
	1773	<0.1	1.4	10.3	44.2	7.4	49.2	70.9

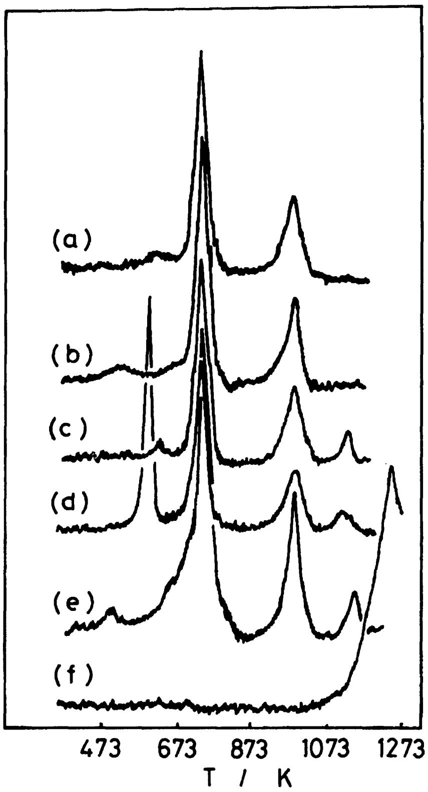


Fig. 2. TGA Spectra of (a) La_2O_3 (precipitated with urea), (b) La_2O_3 (precipitated with Na_2CO_3), (c) Catalyst A, (d) Catalyst B, (e) Catalyst C, and (f) $SrCO_3$.

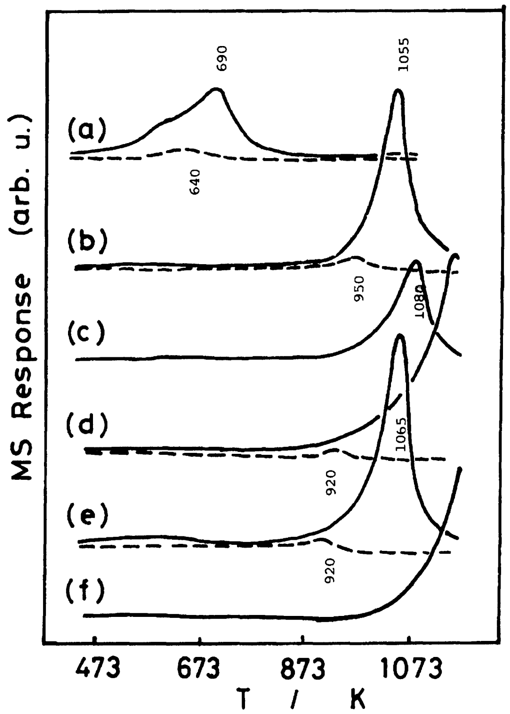
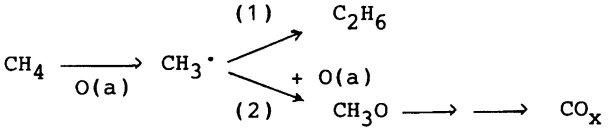


Fig. 3. CO_2-TPD Spectra of (a) La_2O_3, (b) Catalyst A, (c) Catalyst B, (d) Catalyst C, (e) Catalyst E, and (f) $SrCO_3$. Solid and broken lines denote desorption from catalysts calcined at 1173 and 1773 K, respectively. Sr/La=0.2 for Catalyst A—E.

lyst C. These results suggest that the catalyst basicity is slightly affected by the preparation and/or surface morphology, resulting in a variation of the reaction results. The highest selectivity was obtained over Catalyst B calcined at 1173 K.

The low selectivity to C_{2+} hydrocarbons over Catalyst C may be explained in terms of a trace amount of Na on the surface. Owing to residual Na, the basicity evaluated by CO_2-TPD increased. The fact that more basic catalysts, such as $SrCO_3$, are not active at this temperature, suggests that too basic catalysts may be apparently inactive at low reaction temperatures, because the active sites are easily covered with CO_2 under



Scheme 1.

these reaction conditions.[12] Low O_2-conversion gives rise to low selectivity, as reported elsewhere.[13—15]

At $T=1123$ K, however, the preparation method affected the reaction results to a smaller extent, and the yield of C_{2+} hydrocarbons was in a range of 10.1—10.7% over catalysts calcined at 1173 K. The fact that the catalyst basicity (and/or morphology) does affect the reaction results at lower temperatures (as described above), suggests a difference in the relative reaction rates at the elementary steps. The reaction scheme is generally described as follows (Scheme 1): It has been accepted that the desorption of the CH_3 radical, a reaction intermediate, is enhanced at higher temperature. If the desorption (1) is much faster than the surface reaction (2), the secondary reaction on the surface will be unimportant for determining the final product distribution. That may be why the catalyst preparation did not significantly affect the reaction result at $T=1123$ K.

In conclusion, the effect of the catalyst preparation and/or surface morphology was observed when the reaction temperature (T) was as low as $T=973$ K. High C_{2+} selectivity was obtained over the SrO–La_2O_3 catalyst with a columnar shape prepared by a hydrothermal reaction, suggesting that a cetatin plane of the crystal may be responsible for C_{2+} selectivity, as pointed out for other catalysts, such as Sm_2O_3, MgO, and Na_2WO_4/SiO_2.[16—20] A higher C_{2+} yield was obtained at $T=1123$ K than at $T=973$ K, and the effect of catalyst preparation was indistinct at a high reaction temperature. The effects of the pretreatment temperature on the reaction were explained in terms of a change in the catalyst basicity. The formation of a phase with definite basicity and Sr/La ratio was suggested to take place on the surface.

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