

Notes

Catalytic Conversion of Methane to Higher Hydrocarbons over Strontium-incorporated Neodymium Oxide

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The catalytic conversion of methane to higher hydrocarbons such as ethylene and ethane has become an active research area since Keller and Bhasin reported the C₂ hydrocarbon production from methane over metal oxide catalysts in 1982.¹ It has been known that high surface basicity of catalyst is necessary to enhance the C₂ hydrocarbon selectivity in the oxidative coupling of methane and alkali promoters can enhance the basicity of the catalyst.^{2,3} A number of effective catalysts for methane coupling have been reported by many investigators. The promoted lanthanide oxides seem within the most promising catalysts for the reaction. According to the results of Lunsford *et al.*,² hydrothermally treated La₂O₃ and Sm₂O₃ have the largest activities in the oxidative coupling of methane and Nd₂O₃ shows the highest conversion of methane among the lanthanide oxides. Neodymium oxide is known to be a *p*-type semiconductor, represented as NdO_{1.5+x}, and its defect structure can be easily changed to oxygen vacancy by heating it with hydrogen gas. The purpose of this work is to proceed with studies of preparation, physical properties, and catalytic activities of alternative cation-doped neodymium oxides. Recently, we obtained an appreciably better selectivity and yield to higher hydrocarbon products in the oxidative coupling of methane over Sr-doped neodymium oxide catalyst. This letter reports the catalytic conversion of methane to C₂ hydrocarbons and larger amounts of C₃ hydrocarbons at 86% selectivity with 33% methane conversion/pass over Sr-doped neodymium oxide catalyst.

Experimental

Pure neodymium oxide was prepared by decomposition of Nd(NO₃)₃·6H₂O (99.9% pure, Aldrich) at 600 °C which was followed by calcination in flowing oxygen at 1000 °C for 9 hrs. To prepare the strontium-doped neodymium oxide catalysts, Nd(NO₃)₃·6H₂O and Sr(NO₃)₂·4H₂O (99.9% pure, Aldrich) were weighed to give neodymium oxides containing 1, 3, 5, 10, and 20 mol% of strontium, respectively, and mixed together in deionized water at 70 °C. The mixtures were heated at 120 °C with continuous stirring to evaporate excess water until a paste remained. Each mixture was put in an alumina crucible, decomposed at 600 °C for 6 hrs, calcined at 1100 °C for 96 hrs, and then slowly cooled to room temperature. X-ray powder diffractometry for the samples was performed for identification of phase and structure. X-ray photo-

electron spectroscopy (XPS) analyses of the specimens were performed in a PE 5000 ESCA unit to investigate the binding energy of O(1s). The electrical conductivity was measured as a function of Po₂ in the temperature range of 500 to 1000 °C by means of the four-probe technique.⁴

Kinetic measurement was performed using a single-pass flow reactor made of alumina tubing with 1.2 cm o.d and 30 cm length. The grain size of catalysts used in this work was 180-200 mesh and the BET surface areas measured by nitrogen adsorption were in the range of 8 to 11 m²/g. The catalyst was held in the middle of the reactor and the section beyond the catalyst bed in the reactor was filled with alumina beads to reduce the free space. Gas analyses were performed by on-line gas chromatography using a thermal conductivity detector and a flame ionization detector. The purity of gaseous oxygen and methane was greater than 99.99%. The gaseous reactants were purified by passing over a bed of molecular sieve to remove water before introducing them into the reactor. Blank runs were performed over inert alumina beads in the absence of catalyst and approximately 2-4% conversion of methane to CO₂ was obtained in the reaction temperature range of 600 to 800 °C. The major products were CO, CO₂, H₂O, C₂H₄, C₂H₆, C₃H₆, and C₃H₈. Water was removed from the products by a trap placed at the reactor exit. Gas compositions were calculated using external standard gas mixtures prepared by KSRI. The gaseous hydrocarbons were detected by FID after passing through a nickel column packed with Gas Chrome 220, while the other gases such as O₂, CO, and CO₂ were detected by TCD after passing through a Carbosphere column. Following conditions were used to compare the activity of the catalysts: atmospheric pressure, a 0.5 g sample loading of catalyst, a methane-to-oxygen feed mole ratio of 6 without a diluent gas, a feed flow rate at ambient conditions of 17.5 mL/min. The catalyst was pretreated at 400 °C in flowing O₂ for 3 hrs after loading into reactor. The range of reaction temperature explored was 600-800 °C. The conversion of methane was calculated from the amounts of products generated and the methane introduced in the feed stream. The selectivities were calculated on the basis of the conversion of methane to each product and the yield was obtained from the CH₄ conversion and selectivity to each product. The closures on the carbon material balances were within 4%. The conversion of reactants and selectivities to products were typically compared after 3 hrs time-on-stream. No appreciable decrease in catalytic activity and selectivity were observed over extended period of 72 hrs. The details of equipments are described in the previous paper.⁵

Results and Discussion

In this work, Sr-doped neodymium oxide catalysts showed good catalytic activities in the oxidative coupling of methane. Among the catalysts tested, the 10 mol% Sr-doped neodymium oxide catalyst showed the best C₂ yield of 26.8% with a selectivity of 79.5% at 750 °C. Various lanthanide oxide-

Table 1. Catalytic activity and selectivity for oxidative coupling of methane over various lanthanide oxide-based catalysts

Catalyst	Temp. (°C)	CH ₄ conversion (%)	Selectivity (%)			All C _n yield (%)	Ref.
			CO _x	C ₂ ⁺	C ₃ ⁺		
La ₂ O ₃ ^a	700	2.5	49.5	50.5	0	1.3	2
La ₂ O ₃ ^b	750	19.6	40.9	56.6	2.5	11.6	6
Nd ₂ O ₃ ^a	700	4.4	37.5	62.5	0	2.8	2
Nd ₂ O ₃ ^b	750	17.9	43.0	54.0	3.0	10.2	5
Sm ₂ O ₃	700	1.7	44.0	56.0	0	1.0	2
Eu ₂ O ₃	700	18.2	44.1	52.6	3.3	10.2	6
Gd ₂ O ₃	800	19.2	39.0	58.3	2.7	11.7	6
Dy ₂ O ₃	700	0.8	66.0	34.0	0	0.3	2
Li ₂ O ₃ /Sm ₂ O ₃	750	38.0	46.0	54.0	0	20.7	7
1 wt% Li/La ₂ O ₃	800	21.6	24.1	70.2	5.7	16.4	6
1 wt% Sr/La ₂ O ₃	750	20.9	31.0	63.6	5.4	14.4	6
5 mol% Ni/Nd ₂ O ₃	750	27.0	28.9	71.1	0	19.2	this work
8 mol% Mn/Nd ₂ O ₃	750	20.3	56.5	43.5	0	8.8	this work
10 mol% Sr/Nd ₂ O ₃	750	33.7	13.2	79.5	7.3	29.2	this work

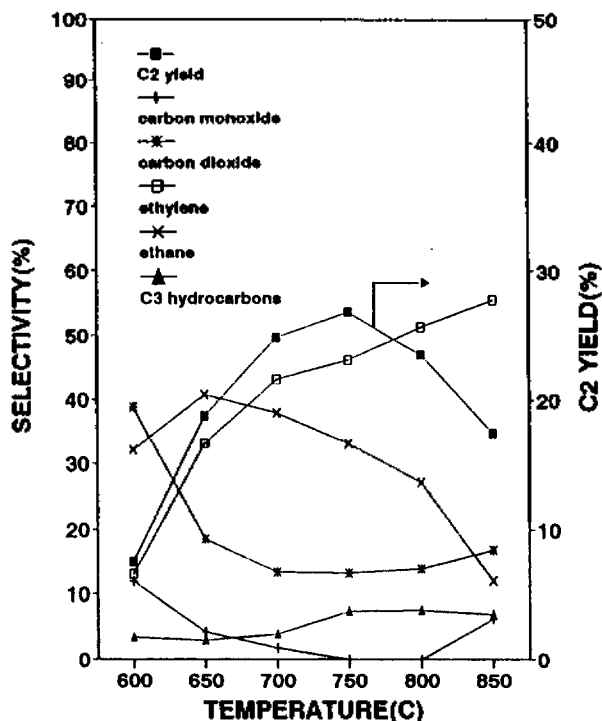
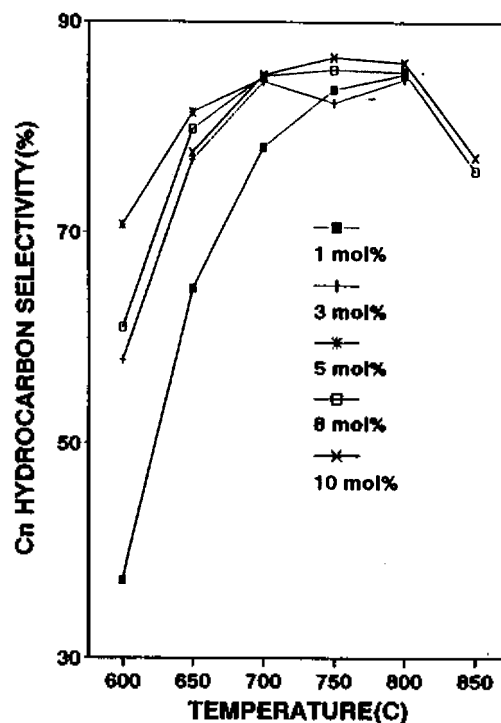
^a Reaction conditions: catalyst weight=5 mg; reaction ratio of CH₄/O₂/He=12.3/1/19.7. ^b Pelletized catalyst (32-52 mesh); P(CH₄)=0.30 atm, P(O₂)=0.05 atm, P(Ar)=0.65 atm; gas hourly space velocity=37500 h⁻¹.

Table 2. Methane conversion and product selectivities on pure Nd₂O₃ and Sr-doped Nd₂O₃ catalysts

Sr loading (mol%)	CH ₄ conversion (%)	Selectivity (%)					All C _n yield (%)
		CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ ⁺	
0	25.5	0	34.5	50.4	15.1	0	16.7
1	26.5	0.7	15.7	44.4	34.1	5.1	22.2
3	28.3	0	17.7	43.7	30.9	7.7	23.3
5	31.0	1.9	13.3	43.5	36.5	4.7	26.3
8	32.4	1.8	12.8	44.2	33.3	7.4	27.5
10	33.7	0	13.2	46.2	33.2	7.3	29.2

Catalyst weight=0.5 g, total feed flow rate=17.6 mL/min, total pressure=1 atm, CH₄/O₂ feed mole ratio=6, and reaction temperature=750 °C.

based catalysts which show more salient catalytic activities and hydrocarbon selectivities in the oxidative coupling of methane are listed in Table 1. Table 2 shows the methane conversion and product selectivities over SrO, Nd₂O₃, and various Sr-incorporated neodymium oxide catalysts, in which pure Nd₂O₃ prepared in this work has a C₂ selectivity of 65.5% and the value is rather appreciable. Both the C₂ yield and the C₂ selectivity were increased with increasing the concentration of Sr-dopant up to 10 mol%. It is interesting to note that C₃ hydrocarbons such as propene and propane were not produced on pure Nd₂O₃, but significant amounts of C₃ hydrocarbons were produced on Sr-doped neodymium oxides. Figure 1 shows variations of C₂ yield and product selectivities with temperature over 10 mol% Sr-doped neodymium oxide catalyst, in which the curve of C₂ yield is a typical volcano type and the C₂ yield maximum is observed

**Figure 1.** Variations of methane conversion and product selectivities with temperature on 10 mol% Sr-doped Nd₂O₃ catalyst (total feed flow rate=17.5 mL/min, n(CH₄)/n(O₂)=6).**Figure 2.** Variations of higher hydrocarbons (C_n) selectivity with temperature on various Sr-doped Nd₂O₃ catalysts (total feed flow rate=17.5 mL/min, n(CH₄)/n(O₂)=6).

at 750 °C. Figure 2 shows the effect of temperature on the selectivity to higher hydrocarbons (C_n) over Sr-doped neodymium oxide catalysts, in which the C_n selectivity increases

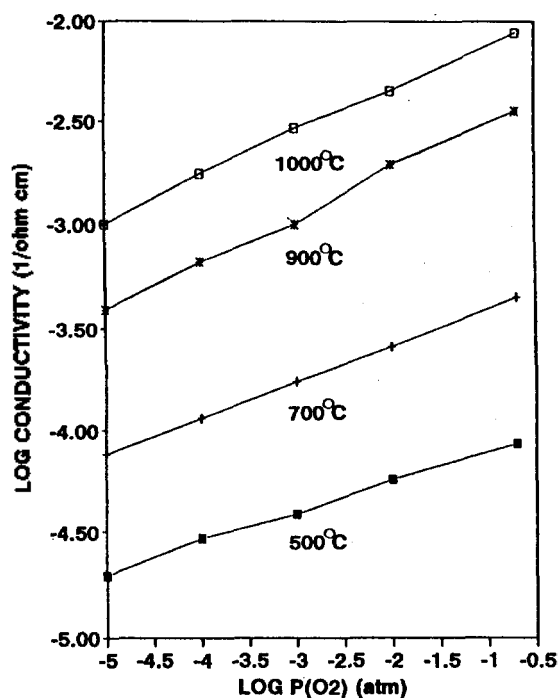


Figure 3. Electrical conductivity as a function of P_{O_2} for 10 mol% Sr-doped Nd_2O_3 .

with increasing the concentration of Sr-dopant and the C_r selectivity maxima of the catalysts are observed around 750 °C.

The lattice parameters obtained from the X-ray diffraction patterns for pure Nd_2O_3 prepared in this work were $a=3.828$ and $c=6.016$ Å and the values are reasonably agreed with the values, $a=3.831$ and $c=5.999$ Å, listed in ASTM. As reported in the previous paper,⁸ a plot of lattice parameters vs dopant Sr mol% showed a good linearity with increasing dopant mol%. The linear increase in the lattice parameters for the hexagonal phase of Sr-doped Nd_2O_3 is in agreement with the result of Lopato *et al.*,⁹ which can be explained by the fact that the ionic radius of Sr^{2+} (1.13 Å) is larger than that of Nd^{3+} (1.08 Å). XRD analyses showed that 1, 3, 5, 8, and 10 mol% Sr-doped Nd_2O_3 specimens completely formed solid solutions, but SrO phase was detected in 15 mol% and 20 mol% Sr-incorporated Nd_2O_3 specimens. The O(1s) XPS spectra of pure Nd_2O_3 and 10 mol% Sr-doped Nd_2O_3 obtained with an effective resolution of 1.0 eV and ± 0.2 eV precision showed two bands. The O(1s) binding energies were observed at 529.9 eV (FWHM 1.96 eV) and 532.4 eV (FWHM 2.34 eV) for pure Nd_2O_3 , and 528.3 eV (FWHM 1.35 eV) and 531.0 eV (FWHM 2.24 eV) for 10 mol% Sr-doped Nd_2O_3 . It has been known that the O(1s) binding energy due to OH^- ions is higher than that due to lattice oxygen (O_l) in metal oxides. Therefore, it is believed that the lower binding energy arises from lattice oxygen of the oxide and the higher binding energy is due to OH^- ions. Since the electron pair donating ability of oxides is assumed to be expressed by the O(1s) binding energy, the O(1s) binding energy of metal oxide is a measure of basic strength of metal oxide and the basic strength increases with decreasing the O(1s) binding energy.¹² In this work, the O(1s) binding energy (528.3 eV) of 10 mol% Sr-doped Nd_2O_3 is lower

than that (529.9 eV) of pure Nd_2O_3 , which means an increase of the basic strength with Sr-doping. The electrical conductivities of Sr-doped neodymium oxides were measured in the range from 500 to 1000 °C at various oxygen partial pressures. The electrical conductivity increased with increasing temperature and the concentration of Sr-dopant, which indicates an Sr-doping effect on the electrical conduction in the oxide. The activation energies obtained from the conductivity-temperature data of Sr-doped neodymium oxides were in the range of 1.40–1.49 eV. Figure 3 is the plot of conductivity variation of 10 mol% Sr-doped Nd_2O_3 system with P_{O_2} in the range of 500 to 1000 °C. The electrical conductivity increases with increasing the P_{O_2} , indicating the specimen to be a p -type semiconductor.

Although various models of methane oxidative dimerization in the presence of metal oxide catalysts have been proposed and the nature of the active species remains to be determined,^{10,11} it is generally accepted that the O^- species on the surface of metal oxide catalyst selectively activate methane in the reaction. According to the FT-IR study of dioxygen adsorption on reduced cerium oxide by Onish *et al.*,¹³ superoxide species are formed immediately after O_2 introduction and successively converted into O_2^{2-} , O^- , and finally into O^{2-} (latt). When methane reacts with active O^- species on the surface of metal oxide, methyl radical is generated and OH^- is simultaneously formed. It has been known that p -type metal oxide semiconductors are effective catalysts in the oxidative coupling of methane under normal operating conditions. It is expected that an altrivalent cation doping into a p -type metal oxide can enhance the p -type character of the oxide, which leads to an enhancement of catalytic activity of the oxide. As shown in Table 2, pure neodymium oxide used in this work showed a catalytic activity in the oxidative coupling of methane. In general, when oxygen molecules are chemisorbed on p -type metal oxide semiconductors such as NiO, PbO, and Nd_2O_3 up to the saturation level while chemisorbing little of the reducing gases such as methane and hydrogen, the metal oxides tend to increase p -type defects such as metal vacancy and electron hole.¹⁴ Therefore, it is believed that the catalytic activity of neodymium oxide arises from its excess oxygen structure. Excess oxygens in neodymium oxide can exist in the form of interstitial oxygen atoms or ions. The neutral interstitial oxygen atoms may in principle be ionized to yield electron holes and oxygen ions with negative effective charges and then, a p -type conductivity of the oxide can be observed. The Sr-doped neodymium oxides used in this work were found to be p -type semiconductors. Both the electrical conductivity and the catalytic activity increased with increasing the Sr mol%, which indicates that the concentration of electron hole increases with Sr-doping and the catalytic activity is influenced by the defects formed by Sr-doping. When Sr^{2+} ions are doped into neodymium sesquioxide, oxygen vacancies can be generated as charge-compensating defects and the oxygen vacancy can act as an adsorption site for oxygen molecule. The oxygen species chemisorbed on the surface of metal oxide can be incorporated into the lattice at high temperatures. If the oxygen incorporation into the oxide becomes predominant, electron holes can be generated by the ionization of metal vacancy and then, the specimen has a p -type conductivity as shown in Figure 3. The results of

electrical conductivity and catalytic activity indicate that the oxygen vacancies formed by Sr-doping into neodymium oxide play an important role on the enhancement of catalytic activity in the oxidative coupling of methane. In Table 1, the Sr-doped Nd_2O_3 shows higher C_n selectivity and methane conversion than Mn^- and Ni-doped Nd_2O_3 systems. Therefore, it is obvious that in the present catalysts, the Sr-doping effect on the production of higher hydrocarbons is more significant than Ni- and Mn-doping effects. Since Ni and Sr have the same valency of 2+ in their oxides, we can not exclude a chemical effect on the catalytic activity of impurity-doped neodymium oxide as well as an electronic effect. $\text{Ni}/\text{Nd}_2\text{O}_3$ and $\text{Mn}/\text{Nd}_2\text{O}_3$ systems prepared in this work were found to be complete solid solutions up to the doping level of 5 mol% Ni and 8 mol% Mn, respectively. Considering the metal ion solubilities and catalytic activities, it is believed that strontium is better promotor than nickel or manganese. Otsuka *et al.*¹⁵ carried out the kinetic studies on the oxidative coupling of methane over samarium oxide catalyst. They obtained the apparent activation energies for the formation of C_2H_6 from CH_4 and the formation of C_2H_4 from C_2H_6 in the temperature range of 873 to 999 K and the values were 135 kJ/mol and 173 kJ/mol, respectively. Since the apparent activation energy for the formation of C_2H_4 from C_2H_6 is higher than that for the formation of C_2H_6 from CH_4 , the ratio of $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$ will be increased with increasing temperature. As shown in Figure 1, the ratio of $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$ increases with increasing the reaction temperature up to 850 °C. The result enable us to consider that ethylene is stepwise produced. Namely, methane is activated *via* abstraction of a hydrogen atom by active oxygen species on the surface of catalyst and the resultant methyl radicals are coupled to form ethane. Ethylene is subsequently produced by dehydrogenation of ethane, not directly produced from methane.

Work is currently in progress to attempt to increase the C_n selectivity and the ratio of $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$. Studies on the surface chemistry and the mechanism of this reaction are also under way.

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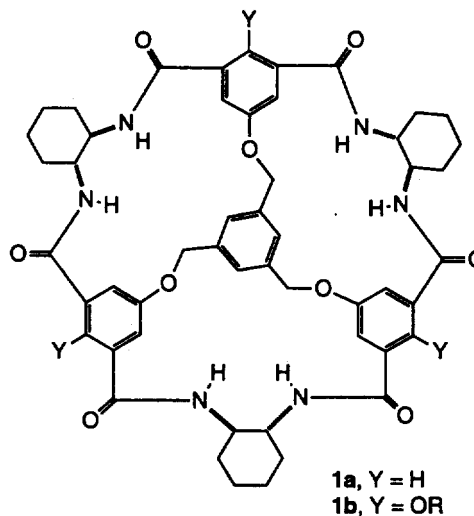
Synthesis of a Novel Basket-Shaped C_3 Receptor

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A major problem in the production of new molecular receptors is the design of structures which form well-defined cavities of dimensions sufficient to encapsulate polyatomic substrates. While monocyclic large ring compounds are generally better hosts than their acyclic counterparts, most of them exist as a multitude of conformations. This conformational flexibility leads not only to reduced binding constants but also to poor selectivities among substrates. To further limit the number of accessible, low energy conformations, bridged macrocyclic systems may be used. While many such molecules having small cavities have been described, only a few structures have been reported with the large binding sites close to those of the active sites of biopolymers.¹



As new structures which are capable of encapsulating large, functionalized substrates (e.g., alanine, serine, valine,