

Total oxidation of methane over perovskite-type complex oxides

$\text{LaFe}_{1-y}\text{A}_y\text{O}_{3-\lambda}$ (A = Mn, Co, Ni)

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It is found that nanometre-particle size oxides $\text{LaFe}_{0.9}\text{A}_{0.1}\text{O}_{3-\lambda}$ (A = Mn, Co, Ni) containing high-valent cations exhibit excellent catalytic activity for the total oxidation of methane at low temperatures.

Numerous advances dealing with perovskite-type oxide catalysts have been made in recent years.¹⁻⁴ There is general agreement that the oxygen species on the surface of catalysts play an important role in the rate-limiting step of methane activation.^{4,5} Vooorhoeve⁶ introduced the terms suprafacial and intrafacial catalysis, which corresponded to low-temperature reactions with adsorbed oxygen (O_{ads}) and high-temperature reactions with lattice oxygen (O_{lat}), respectively. The results of kinetic studies also suggest that the oxidation of methane consists of parallel reactions of adsorbed and lattice oxygen.⁷ It is generally considered that the adsorbed oxygen is responsible for total oxidation, and lattice oxygen for selective oxidation.⁸ However, recent studies^{9,10} show that the lattice oxygen may also result in the total oxidation of methane.

The above conclusions were obtained by studying perovskite-type oxides of large particle size; it is known that mixing of the B-site metals may invoke a synergistic effect^{4,11} and the resulting nanometre-sized materials having unique physical and chemical properties. In our previous report,¹² nanometre-sized perovskite-type complex oxides $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\lambda}$ were first prepared by a sol-gel method, and exhibited higher catalytic activity for the total oxidation of methane than their counterparts of large particle size. In order to improve the catalytic activity and resolve some of the still open questions concerning the mechanism of oxidation of methane, in this work, the nanometre- and large-size perovskite oxides $\text{LaFeO}_{3-\lambda}$ doped with Mn, Co, Ni at B sites were prepared and studied.

All $\text{LaFe}_{1-y}\text{A}_y\text{O}_{3-\lambda}$ (A = Mn, Co, Ni) oxides prepared by the sol-gel method used citric acid as the complexing agent,¹³ and were calcined at 650 °C for 4 h and 900 °C for 2 h for nanometre- and large-size particle samples, respectively. Activity tests were carried out using a continuous flow U-type quartz reactor containing 0.200 g of catalyst. The reaction conditions were $P = 0.1$ MPa, $\text{CH}_4:\text{O}_2 = 1:3.9$, $\text{GHSV} = 18900$ h⁻¹. The catalytic activity was evaluated from the temperature at

which 50% conversion of methane was obtained ($T_{50\%}$) and the specific activity (R) based on the surface area of catalyst. XPS experiments were carried out in an Escalab-MKII system. The C 1s line at 285.0 eV was taken as reference for measurement of the binding energies (E_b) of core level electrons. Prior to the catalytic activity tests and XPS experiments, all samples were treated with an oxygen stream at 650 °C for 1 h. TEM studies were performed with a JEM-100s electromicroscope for the particle size and shape determinations. Temperature programmed reduction (TPR) experiments were performed with a H_2 (5%)- N_2 (95%) mixed gas at a rate of 16 °C min⁻¹.

The results of catalytic activity tests, TEM, XPS and TPR are listed in Table 1. Carbon dioxide was the only detected outlet gas, showing that the oxidation of methane was complete under the selected reaction conditions. It is seen that the $T_{50\%}$ decreased with y up to 0.1, then increased when $y > 0.1$ or with increased particle size suggesting that a synergistic effect between B-site cations existed, resulting in the increase of catalytic activity. The reaction temperature can be lowered significantly by using such substituted nanometre oxides as catalysts.

The catalytic activity may be influenced both by specific area and surface structure of catalysts. According to C 1s spectra, a carbonate peak (*ca.* 289.0 eV) was not detected, suggesting that no carbonate exists on the surface of catalysts treated with oxygen. After smoothing and subtraction, the C 1s envelopes were deconvoluted into two peaks, corresponding to surface adsorbed oxygen and lattice oxygen species, in accord with the literature.¹⁰ It can be seen that the order of specific activity qualitatively follows the ratio $\text{O}_{\text{lat}}:\text{O}_{\text{ads}}$, suggesting that the lattice oxygen favours formation of the total oxidation product. The highest ratios of $\text{O}_{\text{lat}}:\text{O}_{\text{ads}}$ were observed for $\text{LaFe}_{0.9}\text{A}_{0.1}\text{O}_{3-\lambda}$, suggesting that the interaction between cations at B sites may promote the formation of $\text{M}^{(4-\delta)+}$ cations (M = Fe, Mn, Co, Ni) at least on the surface of the catalysts. There appear to be less oxygen vacancies in nanometre-sized oxides relative to their large particle-size counterparts.

The results were further confirmed by TPR experiments. The reduction peaks in the region of 300–500 °C, which can be assigned to the reduction $\text{M}^{(4-\delta)+} \rightarrow \text{M}^{3+}$, shifted to higher

Table 1 Results of catalytic activity tests, TEM, XPS and TPR measurements

Sample $\text{LaFe}_{1-y}\text{A}_y\text{O}_3$		Average size/nm	$T_{50\%}/^\circ\text{C}$	R^a	O 1s Binding energy/eV			$T^b/^\circ\text{C}$	$S_{\text{BET}}/\text{m}^2$ g^{-1}
A	y				O_{lat}	O_{ads}	$\text{O}_{\text{lat}}/\text{O}_{\text{ads}}$		
Fe ^c	0	22	555	1.0	529.5	531.8	1.55	425	22.0
Mn ^c	0.1	20	419	8.5	529.7	532.0	8.50	336	16.0
Mn ^d	0.1	100	617	1.7	529.8	532.3	3.90	377	4.6
Co ^c	0.1	28	411	10.0	529.6	532.0	9.80	313	16.5
Co ^d	0.1	300	555	2.9	529.6	532.0	2.20	498	5.7
Ni ^c	0.1	20	417	6.8	529.3	531.8	4.20	328	22.5
Ni ^d	0.1	345	476	2.7	529.2	531.8	1.20	361	2.7

^a Specific activity, CH_4 converted $\times 4.72 \times 10^{-5}$ mmol s⁻¹ (m² catalyst)⁻¹ at 400 °C. ^b Temperature of reduction peak in low-temperature region.

^c Nanometre-sized oxides calcined at 650 °C. ^d Large particle size oxides calcined at 900 °C.

temperatures with increased particle size or without substitution at B sites, revealing that the reduction of $M^{(4-\delta)+}$ cations becomes more difficult; this can be attributed to the decrease of valence and amount of $M^{(4-\delta)+}$ cations in the large particle size oxides.

It has been reported that in the $La_{1-x}Sr_xFeO_{3-\lambda}$ ¹⁴ and $La_{1-x}Sr_xCoO_{3-\lambda}$ ¹⁵ systems, the oxygen involved in the oxidation reaction reflected the nature of the lattice oxygen, the chemical potential and reactivity of lattice oxygen increasing with formation of unstable Fe^{4+} or Co^{4+} cations. Therefore, the higher $M^{(4-\delta)+}$ content in nanometre-sized oxides $La-Fe_{0.9}A_{0.1}O_{3-\lambda}$ also results in higher catalytic activity, especially at low temperature. It is probable that the activation of methane occurs mainly at $M^{(4-\delta)+}-O^{2-}$ sites at low temperature, and at $M^{3+}-O^{2-}$ sites at high temperatures.

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