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Catalytic property of $A^{II}_2B^{II}B^{VI}O_6$ double perovskites (B^{VI} = Mo, W) for the reduction of nitric oxide with propane in the presence of oxygen

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Abstract

Systematic series of double perovskites containing W and Mo, $A^{II}_2B^{II}B^{VI}O_6$ (A^{II} = Ba, Sr, Ca; B^{II} = Mg, Ca, Co, Ni, Cu, Cd; B^{VI} = W, Mo, $W_{1-x}Mo_x$) were synthesized, and their catalytic activities for NO–C_3H_8–O_2 reaction were investigated. All the oxides crystallized in the ordered double perovskite structure with the rock-salt arrangement of B^{II} and B^{VI} cations, and the unit cell symmetry was almost exclusively determined by A^{II} cations. The double perovskites catalyzed the nonselective reduction of NO into N_2O and occasionally N_2 specifically at 600°C in the gaseous mixture of NO (0.44%), C_3H_8 (0.29%) and O_2 (4.4%). The reduction activity of NO into N_2O and N_2 depended on the sort of A^{II}, B^{II}, and B^{VI} cations, but the effect of B^{II} cations was the most remarkable. The NO reduction activity increased monotonically with an increase in the enthalpy of formation of $B^{II}O$ ($-\Delta H_f°$), suggesting that the strength of B^{II}–O bond or the redox property of B^{II} ions is of primary importance for the NO reduction activity in the NO–C_3H_8–O_2 reaction. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Oxides; D. Catalytic properties; D. Crystal structure

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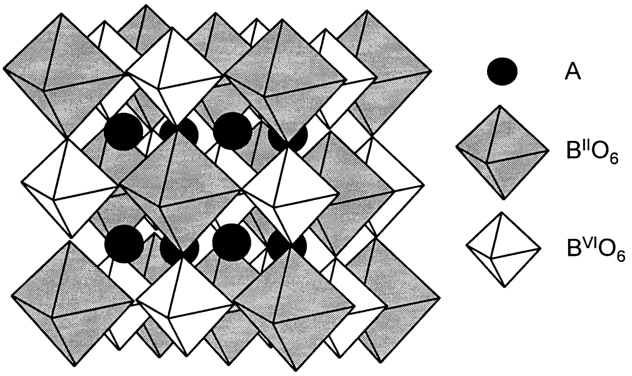

Fig. 1. Structure of $A^{II}_2B^{II}B^{VI}O_6$ double perovskites with the rock-salt ordering of B^{II} and B^{VI} cations.

1. Introduction

Perovskite-type oxides, which have general formula of ABO_3, are an important class of catalytic materials and have been studied extensively as catalysts for complete oxidation of hydrocarbons, direct decomposition of NO, and nonselective reduction of NO by CO, H_2, and hydrocarbons [1–4]. In addition, many basic studies have been carried out to elucidate relationships between the solid-state chemistry and the catalytic properties of perovskite-type oxides [1–4]. So far, both unsubstituted (ABO_3) and substituted ($A_{1-x}A'_xBO_3$, $A_{1-x}A'_xB_{1-y}B'_yO_3$, etc.) systems have been investigated, almost all of which contain rare earth cations, especially La, at the A sites and 3d transition metal ions, especially Co and Mn, at the B sites.

A subclass of perovskites represented by $AA'BB'O_6$ are referred to as a double perovskite in which three B-cation sublattice types are possible: random, rock-salt, and layered [5]. It is known that hexavalent Mo and W (B^{VI}) are stabilized in the ordered double perovskites with the rock-salt arrangement of B^{VI} and divalent B^{II} ions [5,6]. Fig. 1 shows the crystal structure of $A^{II}_2B^{II}B^{VI}O_6$ ordered double perovskite. In this structure, only the three-dimensional chain of the $–B^{II}–O–B^{VI}–O–$ linkage is possible. This specific arrangement of B^{II} and B^{VI} cations is of great interest, because the catalytic properties of perovskites are generally determined by the nature of B-site cations [3]. To the best of our knowledge, however, the work by Voorhoeve et al. [7] is the only report dealing with the catalytic properties of the ordered double perovskite; they reported the catalytic activity of Ba_2CoWO_6 for CO oxidation and NO reduction by CO and H_2. In order to explore new perovskite catalysts as well as to collect more information about the relationships between solid-state chemistry and the catalytic properties, the systematic synthesis and evaluation of catalytic activity of ordered perovskites are highly desired.

Systematic series of $A^{II}_2B^{II}WO_6$ compounds have been already reported with A^{II} = Ba and Sr and B^{II} = Mg, Ca, Co, Cu, Fe, Ni, and Zn [5,6]. In addition, we have recently succeeded the synthesis of systematic series of Mo-containing oxides, $A^{II}_2B^{II}MoO_6$ and $A^{II}_2B^{II}W_{1-x}Mo_xO_6$ [8]. In this paper, catalytic activities of Mo- and W-containing double

Table 1
Ordered double perovskites used in this study[a]

Cubic ($2a_p$ type)[b]	
$Ba_2B^{II}WO_6$	$Ba_2B^{II}MoO_6$
B^{II} = Mg (1250°C, 30 h)	B^{II} = Mg (1250°C, 5 h)
B^{II} = Ca (1100°C, 10 h)	B^{II} = Ca (1200°C, 10 h)
B^{II} = Co (1000°C, 5 h)	B^{II} = Co (1000°C, 20 h)
B^{II} = Ni (1100°C, 30 h)	B^{II} = Ni (1000°C, 5 h)
B^{II} = Cd (900°C, 20 h)	B^{II} = Cd (900°C, 40 h)
	$Ba_2CdW_{0.5}Mo_{0.5}O_6$ (900°C, 30 h)
Tetragonal ($2a_p$ type)[b]	
Ba_2CuWO_6 (900°C, 40 h)	Sr_2CuWO_6 (950°C, 30 h)
Tetragonal ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ type)[b]	
$Sr_2B^{II}WO_6$	$Sr_2MgW_{1-x}Mo_xO_6$
B^{I} = Mg (1100°C, 30 g)	x = 0.25 (1100°C, 20 h)
B^{II} = Co (1200°C, 20 g)	x = 0.5 (1100°C, 60 h)
B^{II} = Ni (1100°C, 20 h)	x = 0.75 (1100°C, 60h)
B^{II} = Cd (950°C, 40 h)	$Sr_2CoW_{0.5}Mo_{0.5}O_6$ (1200°C, 20 h)
$Sr_2B^{II}MoO_6$	
B^{II} = Mg (1100°C, 60 h)	
B^{II} = Co (1150°C, 25 h)	
B^{II} = Ni (1100°C, 20 h)	
Orthorhombic ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ type)[b]	
Sr_2CaWO_6 (1000°C, 30 h)	Ca_2CoWO_6 (1050°, 30 h)
Sr_2CaMoO_6 (1050°C, 45 h)	Ca_2NiWO_6 (1050°C, 20 h)

[a] Synthesis conditions (temperature, time) are shown in parentheses.
[b] a_p is the cell parameter of cubic perovskite of the primitive ABO_3 type ($a_p \approx 0.4$ nm).

perovskites have been investigated for the reduction of NO by C_3H_8 in the presence of excess oxygen, and the relationship between the catalytic property and oxide composition is discussed.

2. Experimental

2.1. Synthesis and characterization of double perovskites

Polycrystalline powders of double perovskites listed in Table 1 were synthesized from appropriate mixtures of MoO_3, WO_3, and nitrates of other elements. Molybdenum and/or tungsten trioxide was added into a mixed aqueous solution of metal nitrates, and the suspended solution was evaporated to dryness under vigorous stirring. The obtained solid mixture was ground and heat-treated at 350°C for 1 h in order to decompose remaining metal nitrates. After regrinding, the mixture was calcined in air; the calcination temperature and time necessary to obtain single-phase double perovskites are listed in Table 1. Powder X-ray diffraction (XRD) patterns were recorded at room temperature using a

Cu Kα radiation (Rigaku RINT-2200VL, 30 kV, 16 mA). The specific surface areas of catalysts, which were measured by N_2 adsorption at liquid N_2 temperature (BET method), were very small, ranging between 1.0 and 0.2 $m^2 \cdot g^{-1}$.

2.2. Catalytic activity test

The catalytic activity was measured in a fixed-bed flow reactor between 300 and 800°C. A mixture of NO (0.44%), C_3H_8 (0.29%), O_2 (4.4%) and He (balance) was fed to 0.5 g catalyst at a rate of 30 $cm^3 \cdot min^{-1}$; the space velocity was 7000 h^{-1}, or the contact time (catalyst weight/gas flow rate) was 1.0 $g \cdot s \cdot cm^{-3}$. The effluent gas was analyzed by a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC 14B). A molecular sieve 5A column was used to separate NO, O_2, N_2, and CO, and a Porapak N column for CO_2 and C_3H_8. The catalytic activity at a steady state, which was attained after 1 h or more on stream, was evaluated by the following parameters:

- Conversion of NO into N_2 ($X[N_2]/\%) = (2[N_2]_{out}/[NO]_{in}) \times 100$
- Conversion of NO into N_2O ($X[N_2O]/\%) = (2[N_2O]_{out}/[NO]_{in}) \times 100$
- Conversion of C_3H_8 into CO_2 ($X[CO_2]/\%) = ([CO_2]_{out}/3[C_3H_8]_{in}) \times 100$
- Conversion of C_3H_8 into CO ($X[CO]/\%) = ([CO]_{out}/3[C_3H_8]_{in}) \times 100$

The total conversion of NO (X[NO]), which is a sum of $X[N_2]$ and $X[N_2O]$, is also used to discuss the NO reduction activity.

3. Results and discussion

3.1. Crystal structure

Double perovskites with the rock-salt sublattice have unit cells with lattice constants of $2a_p$ or $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is the lattice constant of cubic perovskite of the primitive ABO_3 type ($a_p \approx 0.4$ nm). In the present study, four types of unit cells were discerned, and XRD pattern of the representative sample in each type is shown in Fig. 2. The appearance of superlattice lines, for example, 111, 311, and 511 lines of Fig. 2(a), evidences the rock-salt ordering of B^{II} and B^{VI} cations [5]. As can be seen from Table 1, the unit-cell type of $A^{II}{}_2B^{II}B^{VI}O_6$ is almost exclusively determined by the A^{II} cation; almost all oxides with A^{II} = Ba, Sr, and Ca have the structure of cubic $2a_p$ type, tetragonal $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ type, or orthorhombic $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ type, respectively. Exceptions to this rule are oxides with B^{II} = Cu and $Sr_2CaB^{IV}O_6$. The former crystallizes in the tetragonal $2a_p$-type structure, due to the Jahn–Teller distortion of the Cu^{2+} ion [7]. The structure of $SrCaB^{VI}O_6$, the orthorhombic $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ type, is more distorted than that of other tetragonal $SrB^{II}B^{VI}O_6$ oxides, because the combination of smaller A^{II} (Sr) and larger B^{II} (Ca) gives a smaller tolerance factor or fitness factor [8], which results in the lattice distortion. Details of the crystal structure

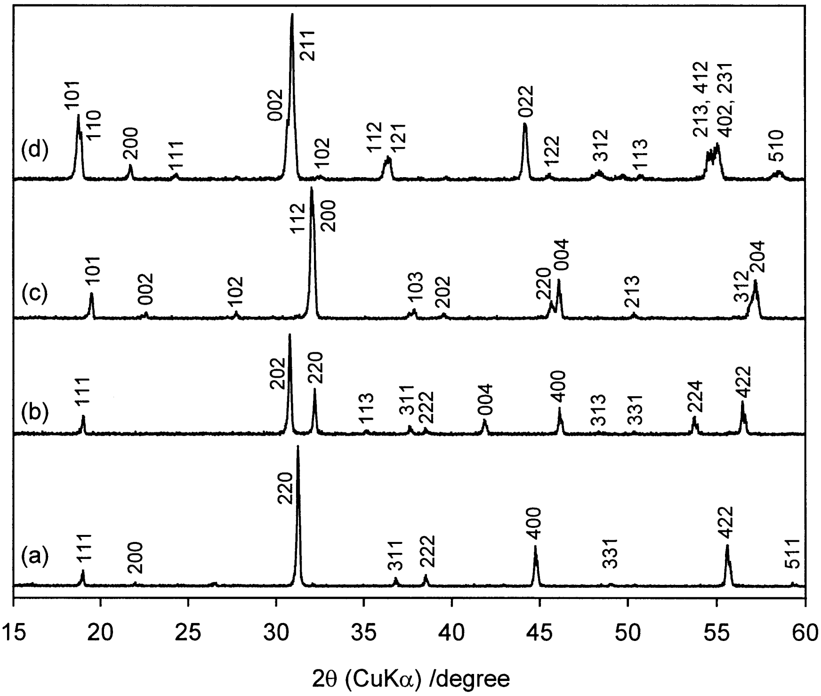

Fig. 2. Powder XRD patterns of double perovskites: (a) cubic $2a_p$-type $Ba_2CoW_{0.5}Mo_{0.5}O_6$, (b) tetragonal $2a_p$-type Ba_2CuWO_6, (c) tetragonal ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$)-type $Sr_2CoW_{0.5}Mo_{0.5}O_6$, and (d) orthorhombic ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$)-type Sr_2CaWO_6.

and cell parameters of the present Mo- and W-containing double perovskites are reported elsewhere [8].

3.2. Catalytic activity

Fig. 3 shows temperature dependence of NO–C_3H_8–O_2 reaction over $Sr_2MgW_{0.5}Mo_{0.5}O_6$ and $Ba_2CoW_{0.5}Mo_{0.5}O_6$. The former is representative of the catalysts showing the higher NO reduction activity with the low conversion of C_3H_8 at 600°C, while the latter is that showing the lower NO reduction activity with the high conversion of C_3H_8. For both catalysts, the reaction proceeded above 500°C, and the reduction of NO into N_2O and N_2 was observed at 600°C. This temperature dependency was common to all the catalysts tested, and, therefore, the catalytic performances at 600°C were used in this study to discuss the catalytic properties of the double perovskites.

Fig. 4 shows the effect of oxygen concentration on the catalytic performance of Sr_2NiMoO_6 at 600°C in the $NO(0.44\%)$–$C_3H_8(0.29\%)$–O_2(variable between 0 and 6.6%) atmosphere. Increasing the O_2 concentration caused monotonic increase and decrease of $X[CO_2]$ and $X[N_2]$, respectively, and the formation of N_2O was observed with the maximum conversion at 2.2% of O_2. In the absence of O_2, only CO_2 and N_2 were detected with the CO_2/N_2 molar ratio being close to 3/5. This indicates the occurrence of the following reaction:

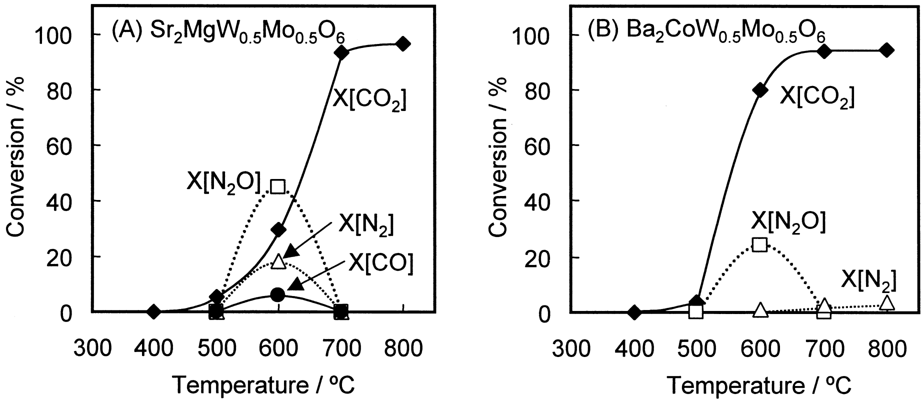

Fig. 3. NO–C_3H_8–O_2 reaction over $Sr_2MgW_{0.5}Mo_{0.5}O_6$ (A) and $Ba_2CoW_{0.5}Mo_{0.5}O_6$ (B). NO(0.44%)–C_3H_8(0.29%)–O_2(4.4%)–He(balance).

$$C_3H_8 + 10NO \rightarrow 5N_2 + 3CO_2 + 4H_2O \tag{1}$$

In the presence of oxygen in the feed gas, the conversion of NO into N_2 decreased progressively with increasing O_2 concentration. This indicates that C_3H_8 reacts with O_2 in preference to NO. At the O_2 concentration of 2.2 and 3.5%, the formation of CO was observed due to the incomplete oxidation of C_3H_8, reaction (2); the conversion of C_3H_8 into CO was 3.6% (2.2% O_2) and 0.6% (3.5% O_2). Assuming that the reduction of NO into N_2O by CO, reaction (3), proceeds rapidly, the enhancement of the N_2O formation at the intermediate O_2 concentration would be reasonably explained.

$$C_3H_8 + (7/2)O_2 \rightarrow 3CO + 4H_2O \tag{2}$$

$$CO + 2NO \rightarrow N_2O + CO_2 \tag{3}$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{4}$$

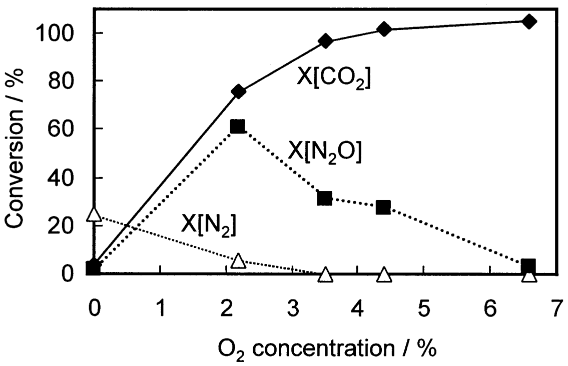

Fig. 4. Effect of oxygen concentration on the catalytic performance of Sr_2NiMoO_6 for the NO–C_3H_8–O_2 reaction at 600°C. NO(0.44%)–C_3H_8(0.29%)–O_2(0–6.6%)–He(balance).

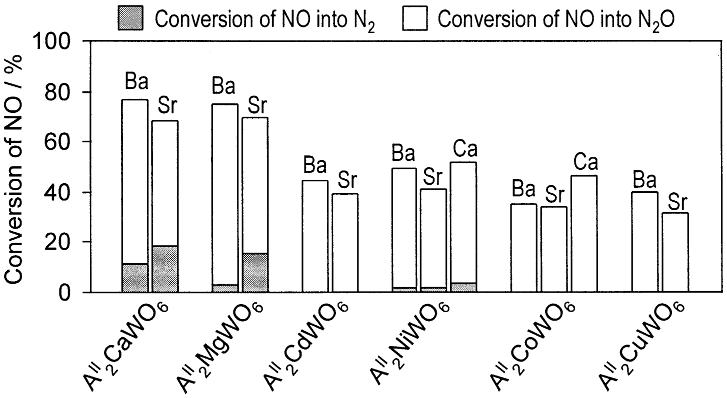

Fig. 5. NO reduction activity of $A^{II}_2B^{II}WO_6$ double perovskites for the NO–C_3H_8–O_2 reaction at 600°C. NO(0.44%)–C_3H_8(0.29%)–O_2(4.4%)–He(balance).

With increasing O_2 concentration, the fraction of C_3H_8 to be completely oxidized, reaction (4), increases, leading to the decrease of the CO formation and thus the conversion of NO into N_2O. The consecutive reaction of $C_3H_8 \rightarrow CO \rightarrow CO_2$ might also be the case; however, this can be regarded as the complete oxidation of C_3H_8. At the highest O_2 concentration (6.6%), the complete oxidation of C_3H_8 by O_2 proceeds exclusively.

The reduction of NO into N_2 by hydrocarbons in the presence of excess oxygen is referred to as the selective reduction of NO with hydrocarbons (HC-SCR). After the pioneering works by Iwamoto et al. [9] and Held et al. [10], the HC-SCR reaction has attracted great attention as a novel NO_x removal process for exhaust treatment. The most characteristic phenomenon of the HC-SCR reaction is that the reduction of NO into N_2 by hydrocarbons is enhanced by coexisting O_2. From this point of view, it can be said that the Mo- and W-containing double perovskites catalyze the nonselective reduction of NO by C_3H_8, but not the HC-SCR reaction.

3.3. Relation between the NO reduction activity and oxide composition

The effect of the A^{II} cation on NO reduction activity is depicted in Fig. 5 for the $A^{II}_2B^{II}WO_6$ series oxides. Nitrous oxide was a main reduction product, and the formation of N_2 was observed only for catalysts with B^{II} = Ca, Mg, and Ni. As can be seen for $A^{II}_2CaWO_6$ and $A^{II}_2MgWO_6$, the oxides with A^{II} = Sr show a higher conversion of NO into N_2 than those with A^{II} = Ba. With regard to the total reduction of NO, which is a sum of conversions into N_2 and N_2O, the Ba compounds show higher activity than the Sr compounds in all the systems. This relation is also true in the $A^{II}_2B^{II}MoO_6$ series oxides. When the Ca compounds are taken into account (B^{II} = Co and Ni), however, the NO reduction activity follows the order of Ca > Ba > Sr. This activity order has no direct relation with ionic radius, Ba > Sr > Ca, or enthalpy of the oxide formation ($-\Delta H_f°$), Ca > Sr > Ba (vide infra). The reason for the effect of the A^{II} cation is not clear at present.

As seen from Fig. 5, the total NO reduction activity depended more largely on B^{II} cations

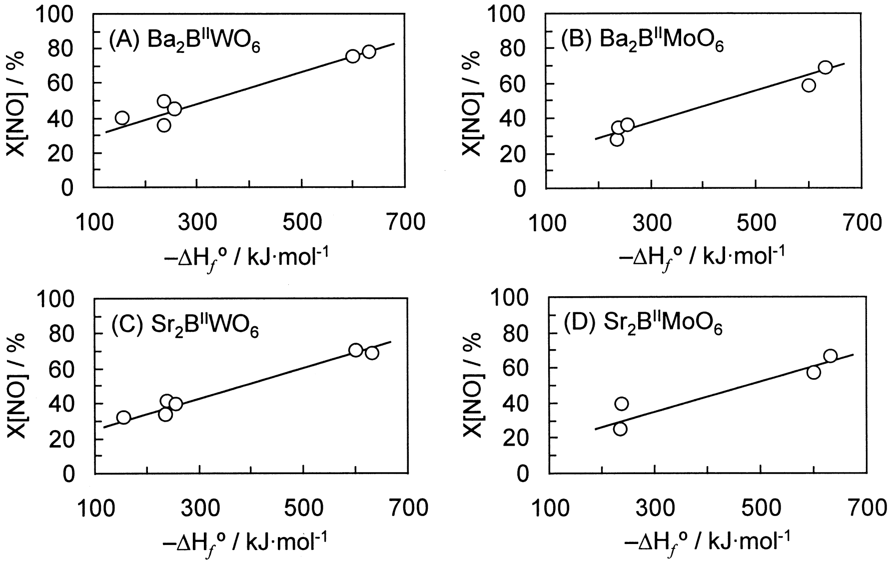

Fig. 6. Relation between the total conversion of NO (X[NO]) and the standard enthalpy of formation of $B^{II}O$, $-\Delta H_f°$. Reaction condition: NO(0.44%)–C_3H_8(0.29%)–O_2(4.4%)–He(balance), 600°C. $-\Delta H_f°/\mathrm{kJ \cdot mol^{-1}}$: 634.9 (CaO), 601.6 (MgO), 258.4 (CdO), 239.7 (NiO), 237.9 (CoO), 157.3 (CuO).

than A^{II} cations, and oxides with B^{II} = Ca and Mg showed higher NO reduction activity than those with 3d transition metal ions, implying that the redox property of the B^{II} ion influences the NO reduction activity. Fig. 6 shows the relationship between the total conversion of NO (X[NO]), and the standard enthalpy of formation of $B^{II}O$, $-\Delta H_f°$ [11,12]. In all of the systems, a good correlation between the two quantities is obtained, and X[NO] tends to increase with increasing $-\Delta H_f°$. In catalytic chemistry, the standard enthalpy of formation of metal oxide per oxygen atom, $-\Delta H_f°$/O-atom, is often used as a parameter of metal–oxygen bond strength, the ability of oxygen activation, or the redox property of metal ions (oxides). For example, it was reported on simple metal oxide catalysts that the catalytic activity for the complete oxidation of propylene [13] and the amount of desorbed oxygen [14] increased with a decrease of $-\Delta H_f°$/O-atom. These results indicate that the ability of oxygen activation increases or the metal–oxygen bond strength weakens with decreasing $-\Delta H_f°$/O-atom. As stated above, the complete oxidation of C_3H_8 by O_2, Eq. (4), competes with the other reactions, Eqs. (1)–(3), to reduce NO into N_2 and N_2O in the present NO–C_3H_8–O_2 reaction system. Accordingly, the tendency observed in Fig. 6 can be expressed in another way that the selectivity to the complete oxidation of propane or the oxidation ability of the catalysts increases with decreasing $-\Delta H_f°$. This is consistent with the above discussion about the relation between $-\Delta H_f°$ and catalytic activity. It can thus be concluded that, when A^{II} and B^{IV} ions are fixed, the catalytic property of $A^{II}_2B^{II}B^{IV}O_6$ in the NO–C_3H_8–O_2 reaction is almost exclusively determined by the redox nature of B^{II} ions, and that the oxide containing B^{II} ion with larger $-\Delta H_f°$ shows a higher activity of, or selectivity to, NO reduction. The comparison between $Ba_2Co^{II}WO_6$ and $Ba_3Co^{III}_2WO_9$ might be significant because both oxides are composed of the same metal cations but contain Co ions

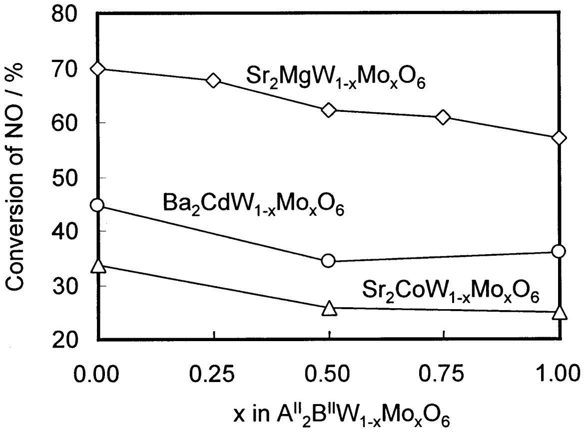

Fig. 7. NO reduction activity of $A^{II}{}_2B^{II}W_{1-x}Mo_xO_6$ double perovskites as a function of the Mo composition x. Reaction condition; NO(0.44%)–C_3H_8(0.29%)–O_2(4.4%)–He(balance).

in different oxidation states. $Ba_3Co^{III}{}_2WO_9$ was prepared by the same procedure as for $Ba_2Co^{II}WO_6$ and had an ordered structure with a 1:2 arrangement of W and Co layers. $Ba_3Co^{III}{}_2WO_9$ was more active than $Ba_2Co^{II}WO_6$ for the complete oxidation of C_3H_8 by O_2 (C_3H_8–O_2 reaction), because of the easy redox change between Co^{III} and Co^{II} [15]. Consequently, $Ba_3Co^{III}{}_2WO_9$ showed lower total NO conversion than $Ba_2Co^{II}WO_6$ (14.7% for the former and 35.3% for the latter at 600°C).

Finally, the dependence of catalytic property on W and Mo is discussed. As shown in Fig. 7, the effect of composition of W or Mo is not so large, but the NO reduction activity tends to decrease with an increase in the Mo composition x. This might be explained by the fact that the $-\Delta H_f°$/O-atom of WO_3 (281.0 kJ · mol O^{-1}) is larger than that of MoO_3 (248.4 kJ · mol O^{-1}). Provided that the reaction proceeds via a redox cycle of the catalyst and that oxide ions bridging B^{II} and B^{VI} ions (–B^{II}–O–B^{VI}–) take part in the catalysis, the catalytic property should be dependent on the redox properties of both B^{II} and B^{VI} ions. Thus, when A^{II} and B^{II} ions are fixed, the redox property of B^{VI} ions controls the catalytic activity. Because the $-\Delta H_f°$ value of $B^{II}O$ is more wide-ranging than that of $B^{VI}O_3$, the catalytic activity of the present catalyst systems presumably depends largely on B^{II} ions.

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