Effect of Oxide Composition of Spinel-type Copper Chromites on the Catalytic Activity for the Simultaneous Removal of NOx and Soot Particulate

by

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The catalytic activity of Cu-Cr oxides for the simultaneous removal of NOx and diesel soot particulate has been investigated with special attention being placed on effects of the composition of oxide catalysts. The temperature programmed reaction technique in which the mixture of a catalyst and soot was heated at a constant rate in an $NO + O_2$ gas stream was used to evaluate the catalytic performance. Spinel-type $CuCr_2O_4$ was superior to CuO, Cr_2O_3 and their mechanical mixture in terms of the selectivity to NOx reduction. The catalytic performance of Cu-Cr oxides depended significantly but complicatedly on the Cr/Cu molar ratio as well as the partial substitution of transition metal and alkali metal cations. The effect of preparation method of $CuCr_2O_4$ was also studied. As compared with the conventional acetate process, the citric acid-aided process gave the monophasic $CuCr_2O_4$ spinel at lower temperatures, and the oxides prepared by the citric acid-aided process were more active than those prepared by the acetate process.

1 . Introduction

Nitrogen oxides and soot particulates emitted from diesel engines cause serious problems on human health and global environment. Nitrogen oxides contribute not only to the production of acid rain but also to produce photochemical smog in combination with hydrocarbons under the influence of sun light. Fine soot particulates, which contain mutagenic hydrocarbons, easily reach far down into lung tissue when inhaled, and therefore have a detrimental impact on human health. Because the reduction of both NOx and particulate emissions to the admitted level cannot be accomplished by engine modifications alone, after-treatment processes for the simultaneous reduction of their emissions from diesel exhaust should be developed. Some of preliminary work demonstrated an enhancement of the NO reduction by carbon doped with alkali metals [1 - 3] . These work has led to the current development program to evaluate the simultaneous removal of NOx and soot. The process in which NOx and soot are removed simultaneously, that is, the reduction of NOx by soot in an oxidizing atmosphere ($NO + C + O_2 \rightarrow N_2 + CO_2$) was proposed by Yoshida et al. [4] , and they found that CuO-based oxides were effective for the catalytic reaction. We have already reported [5] that perovskite-type (ABO_3) oxides are also active for the reaction. Cu-Cr oxides are known to have high catalytic activity for the oxidation reaction in mixed hydrocarbon-CO systems [6] , and they appeared to be important candidates for removing automobile exhaust pollutants [7] . In the present study, we have investigated the catalytic activity of the copper chromites for the simultaneous removal of NOx and soot particulates with special attention being placed on effects of the composition of oxide catalysts and the preparation method of catalysts.

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2. Experimental

2.1 Preparation of catalysts

The following raw materials were used for the preparation of oxide catalysts; $Cr(CH_3CO_2)_3$, $Cu(CH_3CO_2)_2$, $LiNO_3$, $K(CH_3CO_2)$, $Na(CH_3CO_2)$, $Mn(CH_3CO_2)_2$, $Co(CH_3CO_2)_2$, $Fe(OH)(CH_3CO_2)_2$ and $SnCl_2$. Since preparation methods sometimes cause the drastic change of the performance of resulted catalysts through the modification of structure, surface area and morphology [8], two kinds of preparation methods were employed in this study. One is "acetate process"; the mixed aqueous solution containing metal ions in a desired proportion was evaporated to dryness with vigorous stirring, followed by grinding, decomposition at about 400 ℃ for 1 h and, unless stated otherwise, calcination in air at 700 ℃ for 4 h. The other is "citric acid–aided process"; citric acid was added into the mixed aqueous solution, and subsequent steps of evaporation, decomposition and calcination were the same as those in the acetate process.
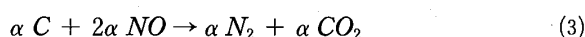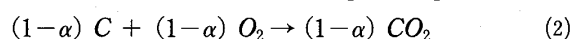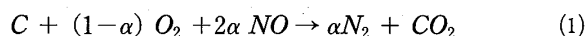
2.2 TG–DTA and XRD

Thermal decomposition behavior of evaporated–to–dryness samples in air was investigated by means of thermogravimetry–differential thermal analysis (TG–DTA; SEIKO TG/DTA 200) at a heating rate of 10 ℃ · min^{-1} between 25 ℃ – 800 ℃. Powder X-ray diffraction (XRD) patterns were recorded on Rigaku 2034 and RINT 2200 diffractometer over the 2θ range of 30 – 70° with Cu Kα radiation (λ = 1.5418 Å).

2.3 Measurement of catalytic activity

Diesel soot particulate was obtained by the incomplete combustion of diesel oil. Since the content of soluble organic fraction (SOF) was less than 5 % in weight, the particulate used in this study was practically "dry soot". The catalyst and the soot (ca. 5 wt%) were well mixed by grinding for 10 min in an agate mortar, then the mixture was pelletized (400 kg·cm^{-2}), crushed, and sieved to 20 – 60 mesh. The catalyst/soot mixture (0.33 g) was placed in a U–shaped quartz–glass reactor, 6.5 mm o.d., and then pretreated in a He flow at 400 ℃ for 3 h in order to eliminate possible contaminants such as adsorbed water; the combustion of soot particulates was reportedly enhanced by the presence of water vapor in gas phase and probably adsorbed water [9]. Catalytic activity was measured with a fixed–bed flow reactor. The reaction gas, usually O_2 [5 %] –NO[0.5%]–He [balance], was obtained by blending three gas flow channels of 10% O_2/He, 1 % NO/He and pure He, and each was controlled by an independent mass flow controller. The catalytic activity was measured by heating the catalyst/soot mixture in a flow of the reaction gas (20 cm^3 · min^{-1}) at a rate of 1 ℃ · min^{-1} (temperature programmed reaction ; TPR). A gas chromatograph with TCD detector was used for the product analysis with intervals of about 15 min. Concentration of CO_2 was directly obtained from peak area of outlet CO_2, and conversion of NO into N_2 was calculated by $2[N_2]_0/[NO]_i$, where $[N_2]_0$ and $[NO]_i$ are concentration of N_2 in outlet gas and NO in inlet gas, respectively.

The overall reaction of the simultaneous removal of NO and soot (C) in the presence of O_2 (Eq. 1) is principally a sum of the oxidation of C by O_2 (Eq. 2) and the oxidation of C by NO to produce N_2 and CO_2 (Eq. 3). In other words, the desirable reduction of NO by C proceeds in competition with the undesirable consumption of C by O_2.

$$C + (1-\alpha)\ O_2 + 2\alpha\ NO \rightarrow \alpha N_2 + CO_2 \qquad (1)$$
$$(1-\alpha)\ C + (1-\alpha)\ O_2 \rightarrow (1-\alpha)\ CO_2 \qquad (2)$$
$$\alpha\ C + 2\alpha\ NO \rightarrow \alpha\ N_2 + \alpha\ CO_2 \qquad (3)$$

In order to evaluate the effectiveness of C for the reduction of NO, the selectivity is defined as the fraction of soot used for reaction 3. The selectivity thus defined is actually equal to α, and can be calculated by Eq. 4.

$$\alpha(\%) = M(N_2)/M(CO_2) \times 100$$
$$or \quad = M(N_2)/M(C) \times 100 \qquad (4)$$

where $M(N_2)$ is the mole number of N_2 produced from NO, $M(CO_2)$ the total mole number of CO_2 produced by the reaction of C with O_2 and NO, and $M(C)$ the mole number of charged soot as carbon. The calculation of selectivity is based on the assumption that the soot consists of only carbon and is oxidized completely to CO_2 but to CO. Actually this was practically the case in the present experimental conditions.

3. Results and Discussion

3.1 Effect of preparation methods

Comparison between the acetate (Ac) and the citric acid-aided (Cit) processes was made for the preparation of Cu-Cr oxide (Cr/Cu=2) in which the expected product was spinel-type $CuCr_2O_4$. Figure 1 shows TG-DTA curves of samples just after the evaporation to dryness in Ac and Cit processes (Ac- and Cit-precursor). Observed in both cases was the one-step weight loss centered at ca. 300 ℃. The larger weight loss and exothermic heat of the Cit-precursor, as compared with the Ac-precursor, indicate that the Cit-precursor contains a certain amount of citric acid probably in the form of citrate complexed with metal cations. Note that the decomposition of the Cit-precursor starts at lower temperature than the Ac-precursor but the temperature for reaching the constant weight is nearly the same between two samples. As can be seen from Table 1, which summarizes crystalline phases detected by XRD for calcined products of Cit- and Ac-precursors, the monophasic $CuCr_2O_4$ spinel was obtained at 600 and 700 ℃ in the Cit and Ac processes, respectively. It was reported in the preparation of perovskite-type oxides [10] that citric acid which has three -COOH groups in one molecule complexed with metal cations to form a precursor keeping the metal cations dispersed homogeneously and that the formation of such a precursor resulted in the lowering of calcination temperature to obtain a monophasic
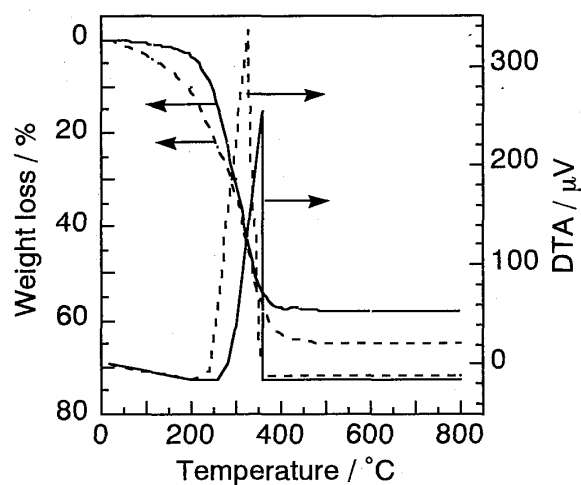
Table 1   Crystalline phases found in Cu-Cr oxides (Cr/Cu=2) prepared by acetate and citric acid-aided process

Calcination temperature/℃	Crystalline phase	
	Acetate process	Citric acid-aided process
400	CuO, Cr_2O_3	CuO, Cr_2O_3
500	CuO, Cr_2O_3	CuO, Cr_2O_3, $CuCr_2O_4$
600	CuO, Cr_2O_3, $CuCr_2O_4$	$CuCr_2O_4$
700	$CuCr_2O_4$	$CuCr_2O_4$

oxide. It seems that the same is the case in the preparation of $CuCr_2O_4$ in this study. Since the formation of monophasic oxides was easier in the Cit process and the process gave more active catalysts as stated later, the Cit process was mainly employed in the preparation of Cu-Cr based oxides.

3.2 Simultaneous removal of NOx and soot particulate

Fig. 2 (a) shows a typical TPR results of the simultaneous removal of NOx and soot over $CuCr_2O_4$. The formation of CO_2 due to the oxidation of the soot and the reduction of NOx into N_2 were observed at the same temperature range. The sudden drops of CO_2 and N_2 formation at higher temperature are of course due to the exhaustion of the charged soot. The curves of CO_2 and N_2 formation were very similar in shape each other. This clearly demonstrates the occurrence of the simultaneous removal of NOx and soot. From Fig. 2 (a), two parameters were derived in order to evaluate the catalytic performance; one is the ignition temperature of soot (T_{ig}) estimated by extrapolating the steeply ascending portion of the CO_2 formation curve to zero CO_2 concentration (estimation error;±5 ℃), and the other is the total amount of N_2 formed throughout the TPR run ($V[N_2]$) obtained by integrating the conversion into N_2 versus temperature (time) curve.

Within the rising portion of CO_2 and N_2 formation curves where the substantial amount of charged soot still remained, Arrhenius-type plots of N_2 and CO_2 formation rates gave straight lines (Fig.2 (b)), indicating that the reaction is thermally well controlled. The apparent activation energy (E_a) was estimated from the slope as a usual manner. The parallelism, that is the nearly the same E_a, between N_2 and CO_2 formation rates suggests that the
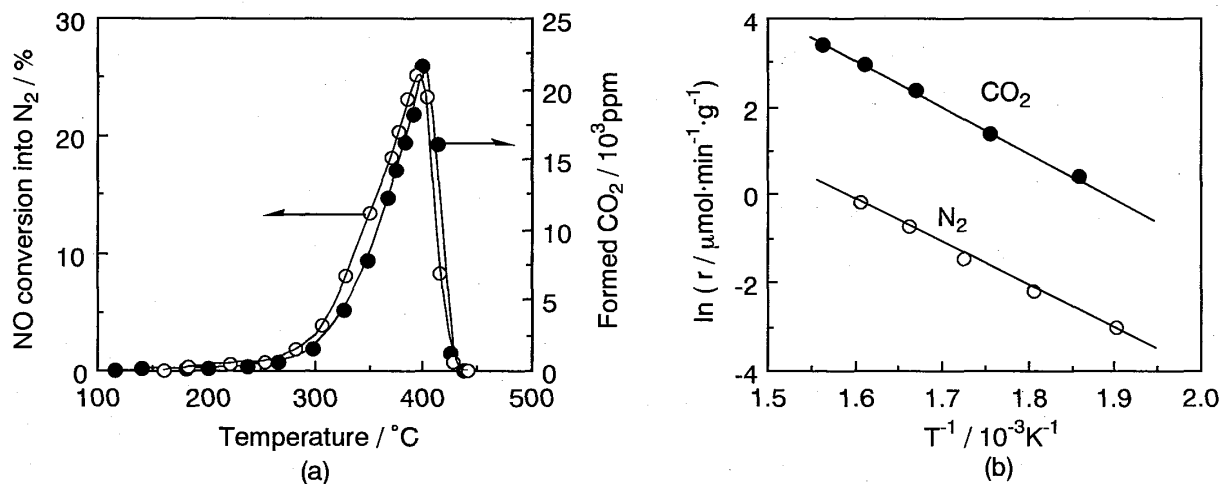

Fig. 1   TG-DTA curves of Cu-Cr oxide precursors (Cr/Cu=2) after the evaporation to dryness in Citric acid-aided (broken line) and Acetate (solid line) processes.

Fig. 2   Simultaneous removal of NOx and diesel soot particulate over $CuCr_2O_4$. (a) Temperature dependence of NOx conversion into N_2 and the outlet concentration of CO_2 during TPR run. (b) Arrhenius–type plots of N_2 and CO_2 formation rates.

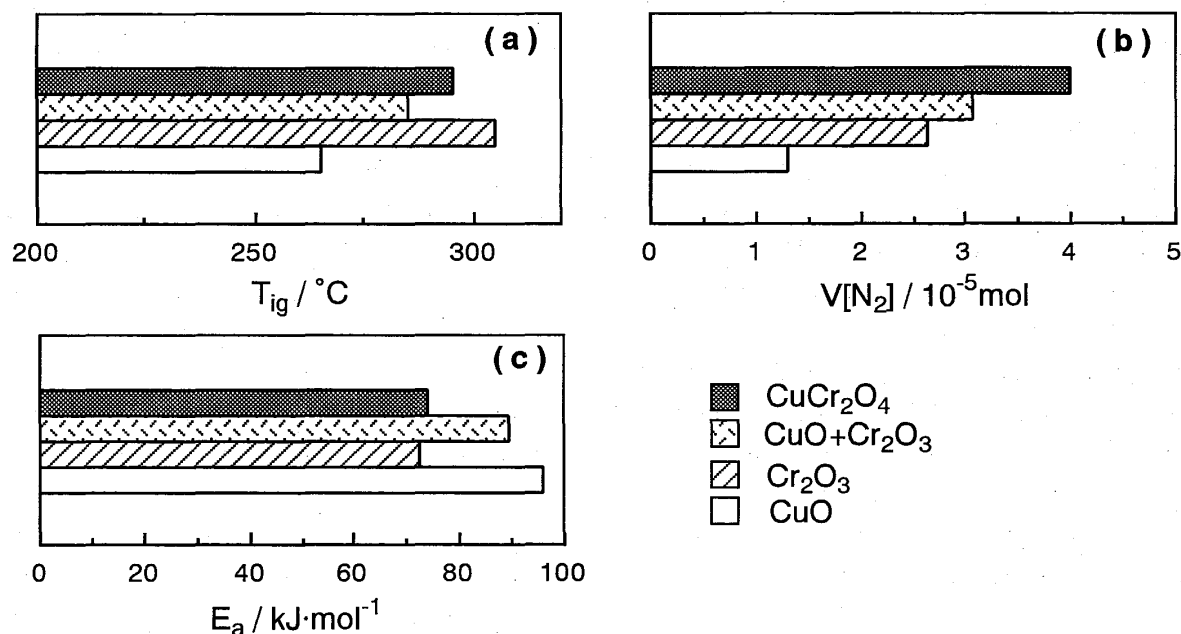Fig. 3   Comparison of ignition temperature of soot (a), total amount of N_2 formed (b), and apparent activation energy for N_2 formation (c) of Cu–Cr oxides.

rate–determining step of N_2 and CO_2 formation is the same. The selectivity to NOx reduction was only 2. 9 % for $CuCr_2O_4$, indicating that the oxidation of the soot by O_2 predominates over that by NOx in the present reaction system.

3 . 3   Comparison between simple oxide, mechanical mixture and spinel oxide of Cu–Cr system

Catalytic activity for the simultaneous removal reaction of simple oxides (CuO, Cr_2O_3) , mechanical mixture ($CuO+Cr_2O_3$, $Cr/Cu=2$ in molar ratio) and

spinel–type oxide ($CuCr_2O_4$) were measured, and three parameters, T_{ig}, $V[N_2]$ and E_a for N_2 formation, were derived from the TPR results (Fig. 3) . T_{ig} was the lowest with CuO, followed by the $CuO+Cr_2O_3$ mixture, spinel–type $CuCr_2O_4$, and Cr_2O_3. The reverse order was the case of E_a. These results indicate that in terms of the catalytic activity the spinel–type oxide and the mechanical mixture containing Cu and Cr lie between active CuO and less active Cr_2O_3 on the whole. As for the selectivity to NOx reduction, on the other hand, catalysts containing Cu and Cr were superior to CuO and Cr_2O_3, indicating

that the coexistence of Cu and Cr ions is essential for the increase in selectivity. In addition, the fact that the selectivity of $CuCr_2O_4$ was higher than that of the $CuO + Cr_2O_3$ implies that an atomically mixed state of Cu and Cr ions such as $-Cu-O-Cr-$ is more effective for activating NOx and/or promoting NOx-C reaction.

It was reported [11] that CuO was more active than Cr_2O_3 for graphite–oxygen reaction. In addition, the E_a value of CuO obtained for the simultaneous removal of NOx and soot, 97.9 kJ·mol^{-1}, is close to that reported for graphite–oxygen reaction ,90.7 or 98.2 kJ·mol^{-1} [11] . These coincidence implies that the activation of carboneous matter by activated oxygen is a key step in both graphite$-O_2$ reaction and the simultaneous removal reaction of NOx and soot; the activated oxygen species naturally originates from molecular oxygen in graphite$-O_2$ reaction, but probably does from NO_2 in the simultaneous removal reaction (see below). The catalytic role of CuO for oxidation of graphite was explained by the redox mechanism [12,13] , in which CuO was reduced by graphite and then regenerated by oxygen. A similar mechanism was also proposed by Ciambelli et al. [14] in the case of soot combustion.

3 . 4　Some factors influencing catalytic activity

3 . 4 . 1　Preparation methods

Figure 4 shows the relation between $V[N_2]$ and T_{ig} of Cu–Cr catalysts with various Cr/Cu ratio prepared by Cit and Ac processes at 700 ℃. Comparing catalysts with the same Cr/Cu ratio (1.5, 1.8, 2.0), it is clear that catalysts prepared by the Cit process were superior to those prepared by the Ac process even when the same calcination temperature was adopted, showing that the Cit process is a promising method for preparing active catalysts.

3 . 4 . 2　Calcination temperature

Compared in Table 2 are some parameters of $CuCr_2O_4$ catalysts prepared by the Cit process at 600, 700 and 800 ℃. As expected, specific surface area decreased with an increase in calcination temperature. The activity judged from T_{ig} deceased with increasing

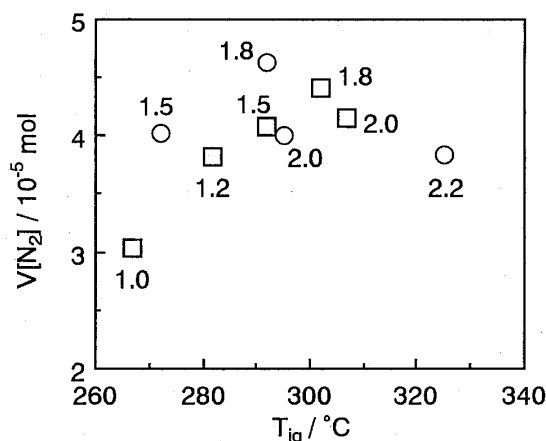Fig. 4　Relation between ignition temperature of soot (T_{ig}) and the total amount of N_2 formed ($V[N_2]$) of Cu–Cr oxides with varying Cr/Cu ratios prepared by Cit (circle) and Ac (square) processes at 700 ℃. The Cr/Cu molar ratios are indicated in the figure.

Table　2　Effect of calcination temperature on catalytic performance of $CuCr_2O_4$ prepared by citric acid–aided process

$T^{1)}$ ℃	$S_a^{2)}$ $m^2·g^{-1}$	$T_{ig}^{3)}$ ℃	$V[N_2]^{4)}$ $10^{-5}mol$	$E_a^{5)}$ $kJ·mol^{-1}$
600	5.7	285	3.1	105.8
700	4.0	295	4.0	80.3
800	2.4	338	3.8	79.6

1) Calcination temperature. 2)　Specific surface area. 3)　Ignition temperature of soot. See text. 4) Total amount of N_2 formed throughout the TPR run. See text. 5)　Apparent activation energy for N_2 formation.

calcination temperature; a small amount of CO was formed over $CuCr_2O_4$ calcined at 800 ℃, but not over the other two catalysts. On the other hand, the total amount of N_2 formed, $V[N_2]$, which is a measure of the selectivity to NOx reduction, was low for catalysts calcined at 600 ℃, and reached a moderate maximum at the catalyst calcined at 700 ℃. Accordingly it is concluded that calcination at 700 ℃, which gives the catalyst with an intermediate T_{ig} (activity) and the highest $V[N_2]$ (selectivity), is optimum for the preparation of $CuCr_2O_4$.

3 . 4 . 3　Cr/Cu ratio

The ignition temperature of soot and NOx reduction to N_2 depended on the molar ratio of Cr/Cu (Fig. 4) . The oxide with Cr/Cu=2 was a monophasic

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$CuCr_2O_4$, and oxides with the Cr/Cu ratio greater and smaller than 2 contained Cr_2O_3 and CuO, respectively, in addition to spinel–type $CuCr_2O_4$. The catalytic activity judged from T_{ig} increased as the Cr/Cu ratio decreased, which can be explained by the activity order of respective phases, $Cr_2O_3 < CuCr_2O_4 < CuO$. The selectivity to NOx reduction ($V[N_2]$), on the other hand, decreased when the Cr/Cu ratio was far from the stoichiometric composition of $CuCr_2O_4$ (Cr/Cu=2) . This can be ascribable to the lower selectivity of CuO and Cr_2O_3 than that of $CuCr_2O_4$ as mentioned above. It is of interest to note, however, that the catalysts with a small excess of CuO (Cr/Cu=1.8) showed the highest $V[N_2]$. Although the reason for this is not clear at the present, the following might be concerned with it; generation of catalytic sites at the grain boundary (contact point) between CuO and $CuCr_2O_4$, formation of a Cu–excess solid solution like $CuCr_{2-x}O_4$.

3.4.4 Substitution

We have reported that the catalytic activity for the simultaneous removal of NOx and soot of perovskite–type oxides changes by the sort and composition of constituent metal cations and that the substitution of alkali metals, especially K, results in the prominent promotion effect with the increasing $V[N_2]$ and decreasing T_{ig} [5] . Accordingly, the effect of partial substitution in the present $CuCr_2O_4$ spinel was also investigated. Catalytic parameters, T_{ig}, $V[N_2]$ and the selectivity to NOx reduction, of $CuCr_2O_4$–based oxides with various substituents are listed in Table 3, and the T_{ig} vs. $V[N_2]$ relation of catalysts except for less active Sn–substituted oxide is shown in Fig. 5. The catalytic performance of these oxides changed significantly depending on both A– and B–site cations as well as the substitution level; a spinel–type oxide is generally expressed as AB_2O_4, and therefore A and B sites mean Cu and Cr sites, respectively, in the present case. Roughly speaking, catalysts substituted by transition metal cations were comparable to unsubstituted $CuCr_2O_4$ with respective to activity and selectivity. The substitution of alkali metal cations, on the other hand, caused an increase in activity (a decrease in T_{ig}) and the effect of B–site substitution was more prominent than that of A–site substitu-

Table 3 Catalytic activities of substituted Cu–Cr spinel–type oxides for the simultaneous removal of NOx and soot particulate

Catalyst[1]	T_{ig}[2]/$°C$	$V[N_2]$[3]/10^{-5}mol	α[4]/%
1 $CuCr_2O_4$	295	4.00	2.9
2 $Cu_{0.9}Li_{0.1}Cr_2O_4$	285	2.11	1.5
3 $CuCr_{1.9}Li_{0.1}O_4$	260	2.36	1.7
4 $Cu_{0.8}Na_{0.2}Cr_2O_4$	280	1.30	0.9
5 $CuCr_{1.8}Na_{0.2}O_4$	268	1.04	0.8
6 $Cu_{0.9}K_{0.1}Cr_2O_4$	282	2.90	2.1
7 $Cu_{0.8}K_{0.2}Cr_2O_4$	280	2.50	1.8
8 $CuCr_{1.95}K_{0.05}O_4$	284	3.77	2.7
9 $CuCr_{1.8}K_{0.2}O_4$	255	2.56	1.9
10 $CuCr_{1.8}Sn_{0.2}O_4$	370	2.93	2.1
11 $CuCr_{1.9}Co_{0.1}O_4$	290	4.57	3.3
12 $Cu_{0.9}Fe_{0.1}Cr_2O_4$	300	4.21	3.1
13 $CuCr_{1.9}Mn_{0.1}O_4$	285	4.60	3.3

1) Prepared by citric acid–aided process at 700 $°C$.
2) Ignition temperature of soot. See text. 3) Total amount of N_2 formed throughout the TPR run. See text. 4) Selectivity to NOx reduction. See text.
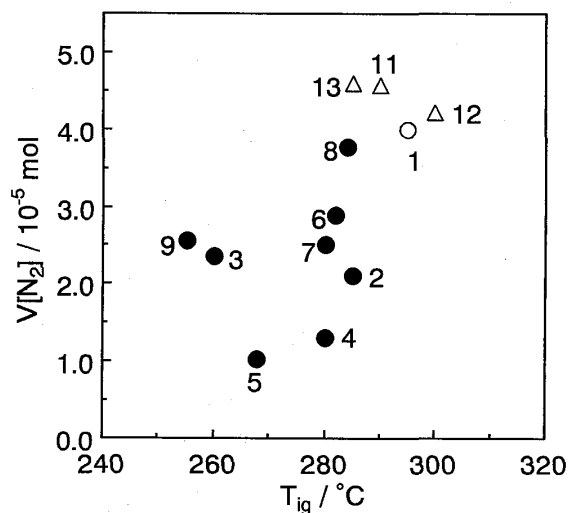

Fig. 5 Relation between ignition temperature of soot (T_{ig}) and the total amount of N_2 formed ($V[N_2]$) of substituted Cu–Cr spinel–type oxides prepared by the Cit process at 700 $°C$. See Table 3 for the listing of catalysts.

tion. However, the substitution by alkali metal ions resulted in a decrease in selectivity, though effects of the sort and the composition of substituted alkali metal cations were not straightforward. The effect of the substitution of alkali metal ions in $CuCr_2O_4$ observed in this study was quite different from that found in perovskite–type oxides [5] . These difference is not due to the crystal structure but to consti-

tuent metal cations, because we have confirmed the promotion effect in spinel–type CuFe$_2$O$_4$ similar to that in perovskite–type oxides [15].

3.4.5 Composition of reaction gas

Reactions of soot with NO and/or O$_2$ were investigated over CuCr$_2$O$_4$ by feeding reaction gases of NO [0.5%] +O$_2$ [5%], O$_2$ [5%], and NO [1%] diluted with He. Because the formation of CO and N$_2$O was not detected, reactions taking place in NO+ O$_2$, O$_2$ and NO gases can be written as Eqs. (1), (5) and (6), respectively.
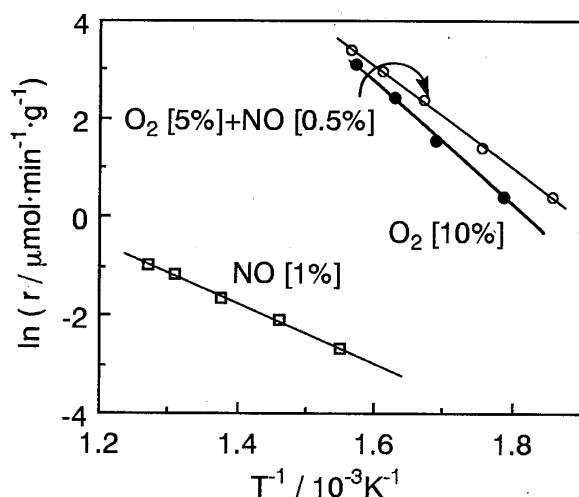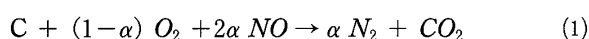
$$C + (1-\alpha)\ O_2 + 2\alpha\ NO \rightarrow \alpha\ N_2 + CO_2 \qquad (1)$$
$$C + O_2 \rightarrow CO_2 \qquad (5)$$
$$C + 2NO \rightarrow N_2 + CO_2 \qquad (6)$$

Fig. 6 Arrhenius–type plots for CO$_2$ formation rate over CuCr$_2$O$_4$ in NO+O$_2$, O$_2$ and NO reaction gases.

It is accepted that the formation rate of CO$_2$ which is a common product is the best measure in order to compare these three reactions. As shown in Fig. 6, the rate for NO–O$_2$–soot reaction is comparable to that for O$_2$–soot reaction, but greater than that for NO–soot reaction, indicating that O$_2$ plays an important role in the simultaneous removal of NOx and soot particulates. The ignition temperature was found to depend also on the reaction gas as NO+O$_2$ (295 ℃) < O$_2$ (325 ℃) < NO (520 ℃). The lowest T$_{ig}$, that is the highest activity, in NO+O$_2$ gas strongly suggests such a mechanism that the reaction is accelerated by the cooperation of NO and O$_2$, for example, the im-

plication of NO$_2$, especially in lower temperature region.

4. Conclusion

Catalytic activity of oxide catalysts in the Cu–Cr–based system was investigated for simultaneous removal of NOx and soot particulates. Results obtained in this study can be summarized as follows.

1) Citric acid–aided process was more effective than the acetate process in the preparation of the spinel–type oxide at lower temperatures. In addition, catalysts prepared by the citric acid–aided process were more active than those prepared by the acetate process even when calcined at the same temperature.

2) The selectivity to NOx reduction of spinel–type CuCr$_2$O$_4$ was superior to that of CuO, Cr$_2$O$_3$ and their mechanical mixture.

3) The activity and selectivity of Cu–Cr oxides depended significantly on the molar ratio of Cr/Cu; the activity increased with a decrease in the Cr/Cu ratio, while the selectivity became maximum at Cr/Cu=1.8.

4) The catalytic performance of CuCr$_2$O$_4$ changed by the substitution at both A(Cu) and B(Cr) sites. Although the effect of the substitution of transition metal ions at B sites was small, the substitution of alkali metal ions at A and B sites resulted in an increase in activity and a decrease in selectivity.

5) The activity of CuCr$_2$O$_4$ depended on the composition of reaction gas and increased as NO < O$_2$ < NO+O$_2$.

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