

## Promoted Ir/SiO<sub>2</sub> Catalysts for the Selective Reduction of NO in the Presence of O<sub>2</sub> and SO<sub>2</sub>

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The effect of metal additives on the catalytic performance of Ir/SiO<sub>2</sub> catalyst for the selective reduction of NO with H<sub>2</sub> in the presence of O<sub>2</sub> and SO<sub>2</sub> was investigated. The addition of alkali and alkaline earth metals was quite effective to enhance the catalytic activity and selectivity of Ir/SiO<sub>2</sub> for NO reduction under the conditions of low temperature and high O<sub>2</sub> concentration. The promoting effect of alkali metals and alkaline earth metals was found to be in the order of Li > Na > K > Rb > Cs, and Ba > Sr ~ Ca > Mg, respectively. Li was the most effective additive. Catalyst characterization suggested that Li prevents catalyst deactivation as an oxidation-retardant for the active Ir metal supported on SiO<sub>2</sub>.

Key words: Nitrogen oxide, Selective reduction, Hydrogen, Iridium silica catalyst, Alkali metal, Alkaline earth metal

### 1. INTRODUCTION

The removal of NO<sub>x</sub> in exhaust emissions is one of the major issues in environmental technology. In particular, the development of catalytic technologies for NO<sub>x</sub> removal in diesel exhaust attracts much attention recently because the three way catalyst system, which works very well for gasoline-fueled vehicles, cannot reduce NO<sub>x</sub> in oxygen-rich diesel exhaust. NH<sub>3</sub>-SCR (selective catalytic reduction), which is another well-known catalytic NO<sub>x</sub> removal system and now employed for large-scale boilers, uses poisonous NH<sub>3</sub> and therefore is not suitable for mobile or small NO<sub>x</sub> sources.

In this regard, several novel catalytic technologies have been under investigation. For instance, urea-SCR<sup>1)</sup>, which uses nonpoisonous urea as a reductant in place of NH<sub>3</sub>, is considered to be a hopeful measure for heavy-duty diesel vehicles. However, the establishment of the infrastructure for urea supply is a practical problem. NO<sub>x</sub> storage-reduction (NSR)<sup>2)</sup> recently developed by Toyota is also an efficient catalytic NO<sub>x</sub> reduction system for diesel vehicles. However, the catalysts used in this system are very sensitive to poisoning by SO<sub>x</sub> contained in diesel exhaust. Sophisticated and complicated engine control is also necessary for this system.

Accordingly, the development of effective catalysts for SCR of NO using more practical reductants other than NH<sub>3</sub> and urea is more desirable from a practical point of view. In this regard, SCR of NO with hydrocarbons in the presence of O<sub>2</sub> has been a focus of attention from lots of researchers for the past decade, and quite a number of active catalysts have been found<sup>3-5)</sup>. Nevertheless, their catalytic activity is not sufficient for application to diesel vehicles in spite of the enormous efforts given to the investigation.

Recently, several papers have been published on the selective reduction of NO using H<sub>2</sub> as a reductant over supported Pt or Pd catalysts<sup>6-9)</sup>. Although these catalysts can reduce NO efficiently in the presence of O<sub>2</sub>, coexisting SO<sub>2</sub> causes a complete loss of catalytic activity. Moreover, the temperature window, in which NO reduction proceeds, is quite narrow. Our group, on the other hand, has recently found that SiO<sub>2</sub>-supported Ir and Rh are active for the selective reduction of NO with H<sub>2</sub><sup>10-12)</sup>. The most prominent feature of this novel catalytic reaction is that the presence of both O<sub>2</sub> and SO<sub>2</sub> is necessary for NO reduction to proceed. This is a quite favorable nature for the treatment of diesel exhaust. Another interesting characteristic of this catalytic reaction is that SiO<sub>2</sub> is the only effective support.

One of the disadvantages of this catalytic reaction is that, although the catalysts show quite high activity, the selectivity at high O<sub>2</sub> concentrations is not sufficient, which should be improved for practical use. In this paper, we wish to report that alkali and alkaline earth metals show an excellent promoting effect on the NO reduction activity of Ir/SiO<sub>2</sub> for the selective reduction of NO with H<sub>2</sub> in the presence of O<sub>2</sub> and SO<sub>2</sub>.

### 2. EXPERIMENTAL

#### 2.1 Catalyst preparation

SiO<sub>2</sub> (Fuji Silysia Chemical, Cariax G-10, 300 m<sup>2</sup>g<sup>-1</sup>) was used as a catalyst support. Ir/SiO<sub>2</sub> was prepared by impregnation of SiO<sub>2</sub> with an aqueous solution of H<sub>2</sub>IrCl<sub>6</sub>, followed by drying at 110°C overnight and calcination at 600°C for 8h in air. The loading of Ir metal was fixed at 5 wt% in this study.

The doping of the alkali metals (Li, Na, K, Rb, and Cs) and alkaline earth metals (Mg, Ca, Sr, and Ba) was performed by impregnation of Ir/SiO<sub>2</sub> with aqueous solutions of nitrate, followed by drying at 110°C

overnight and calcination at 600°C for 8h in air. The loading of the metals was fixed at a molar M/Ir ratio of 1/3 except for Li, in which case the loading was changed from 1/6 to 3/3.

## 2.2 Catalytic activity measurement

The catalytic activity was measured by using a fixed bed flow reactor made of quartz with a 10mm diameter. The standard reaction gas contained 1000ppm NO, 5% O<sub>2</sub>, 6000 ppm H<sub>2</sub>, 6% H<sub>2</sub>O and 20 ppm SO<sub>2</sub> diluted in He, unless otherwise specified.

The standard reaction procedure was as follows. 0.04g of a catalyst placed in the reactor was pre-reduced in a gas flow containing 6000 ppm H<sub>2</sub> and 6% H<sub>2</sub>O in He. After the gas was switched to the reaction gas, stable catalytic activity was measured at each temperature as the reaction temperature was lowered from 600°C with a step of 50°C. In some cases, the activity was measured while the temperature was raised from 200°C to 600°C with a step of 50°C.

The analysis of the effluent gas was made using two gas chromatographs (Shimadzu GC8A) equipped with a Molecular Sieve 5A column (for the analysis of N<sub>2</sub> and H<sub>2</sub>) and a Porapak Q column (for the analysis of N<sub>2</sub>O). The catalytic activity was evaluated in terms of NO conversion to N<sub>2</sub> (and N<sub>2</sub>O) and H<sub>2</sub> conversion. A chemiluminescence NOx analyzer was used to check the stability of the catalytic activity.

## 2.3 Catalyst characterization

X-ray diffraction measurements (Mac Science MXP18) were performed to get information on the crystal structure of the catalyst samples by using CuK $\alpha$  radiation at 40kV and 150mA. The scanning was done from 2 $\theta$ = 10 to 90 degrees at a speed of 5 deg min<sup>-1</sup>.

TPO (Temperature-programmed oxidation) of the catalyst samples was also performed. 0.1g of a sample was first reduced at 400°C in flowing 100% H<sub>2</sub> for 1h and then the gas was switched to He and the temperature was lowered to room temperature in He. Then, TPO was done in a gas flow of 1% O<sub>2</sub>/He at a heating rate of 10°C min<sup>-1</sup> to 800°C. The consumption of O<sub>2</sub> was monitored with a mass spectrometer.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of metal additives

Fig.1 shows the additive effect of alkali metals on the catalytic activity of Ir/SiO<sub>2</sub>. Here, the loading of alkali metals was fixed at M/Ir= 1/3. It is seen that the activity for NO reduction at lower temperatures increases when K, Na and Li was doped to Ir/SiO<sub>2</sub>. Li shows the most prominent effect to promote the activity at temperatures from 200°C to 300°C. The formation ratio of N<sub>2</sub>/N<sub>2</sub>O as the reduction products of NO was approximately 3/1 in most cases (not shown in figures). The activity for H<sub>2</sub> conversion was also promoted by addition of the alkali metals. It is interesting, on the other hand, that Cs, which is the heaviest alkali metal, decreased the activity of Ir/SiO<sub>2</sub> over almost the entire temperature range. Thus, the promoting effect of alkali metal additives was in the order of Li > Na > K > none ~ Rb > Cs.

Fig.2 presents the additive effect of alkaline earth metals. It is quite surprising that, in contrast to alkali metals, heavier alkaline earth metals showed more

promotion effect on Ir/SiO<sub>2</sub>, Ba being the most efficient promoter. On the other hand, Mg deteriorates the activity of Ir/SiO<sub>2</sub> just like Cs. Consequently, the promoting effect of the alkaline earth metals was found to be in the order of Ba > Sr ~ Ca > none > Mg.

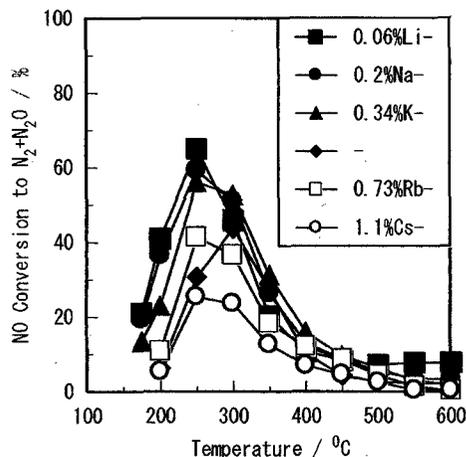


Fig.1 Effect of alkali metal additives

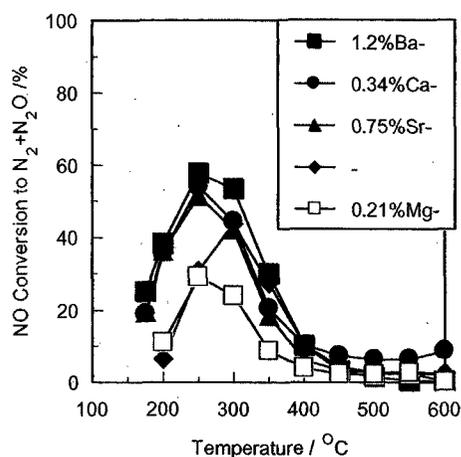


Fig.2 Effect of alkaline earth metal additives

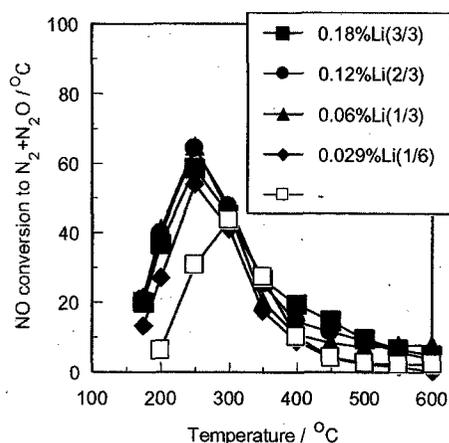


Fig.3 Effect of Li amount on the activity of Li/Ir/SiO<sub>2</sub>

### 3.2 Catalytic performance of Li-promoted Ir/SiO<sub>2</sub>

Since Li was the most effective additive, the performance of Li-promoted Ir/SiO<sub>2</sub> was investigated. In Fig.3 is shown the effect of Li loading on the catalytic

activity of Li/Ir/SiO<sub>2</sub>. Here, the ratio of Li/Ir was changed from 1/6 to 3/3. The NO reduction activity increased with Li loading up to Li/Ir= 1/3. However, the activity was not promoted when Li loading was further increased. H<sub>2</sub> conversion also increased by Li addition up to Li/Ir= 1/3 but remained unchanged after that.

Since this reaction is very sensitive to the presence of O<sub>2</sub>, the catalytic activity of Li/Ir/SiO<sub>2</sub> (Li/Ir= 1/3) was checked in comparison with Ir/SiO<sub>2</sub> by changing the concentrations of O<sub>2</sub> from 0% to 10%. Figs.4 and 5 present the catalytic performance of Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub>, respectively, for NO reduction in the presence of various O<sub>2</sub> concentrations. It should be noted that 20 ppm SO<sub>2</sub> was always present in the reaction gas. In the absence of O<sub>2</sub>, neither Ir/SiO<sub>2</sub> nor Li/Ir/SiO<sub>2</sub> showed any activity for NO reduction from 200°C to 600°C. In the presence of 1% O<sub>2</sub>, the NO conversion was considerably increased on both Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub>. This indicates that O<sub>2</sub> is necessary for NO reduction with H<sub>2</sub> in the presence of SO<sub>2</sub>. With regard to the effect of Li, it is quite interesting that the activity of Ir/SiO<sub>2</sub> is better than that of Li/Ir/SiO<sub>2</sub> for NO reduction in the presence of 1% O<sub>2</sub>. When O<sub>2</sub> concentration was increased to 5% and 10%, however, Li/Ir/SiO<sub>2</sub> showed better activity than Ir/SiO<sub>2</sub>. Accordingly, it can be concluded that the promotion effect of Li was observed only at high O<sub>2</sub> concentrations.

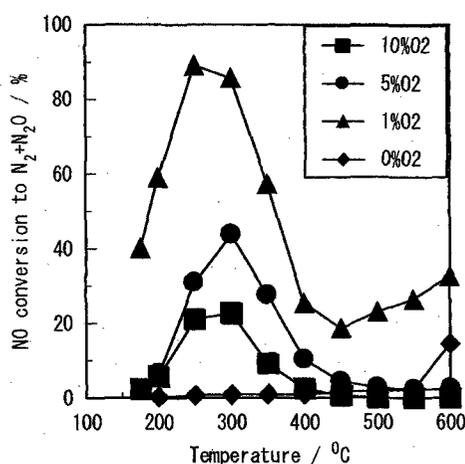


Fig.4 Effect of O<sub>2</sub> on the Activity of Ir/SiO<sub>2</sub>.

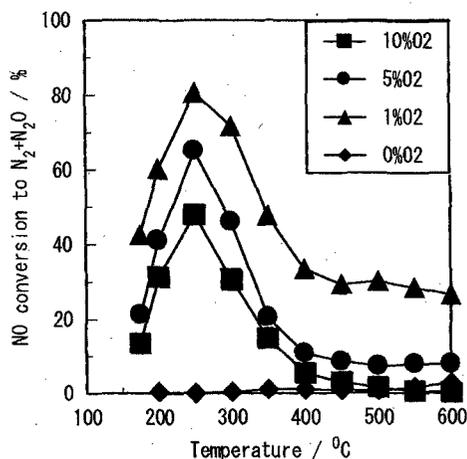


Fig.5 Effect of O<sub>2</sub> on the activity of Li/Ir/SiO<sub>2</sub>.

### 3.3 Role of Li promoter

In order to get information on the role of Li promoter, X-ray diffraction patterns were recorded for Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub>, which are shown in Fig.6. The diffraction lines of IrO<sub>2</sub> were detected for both Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub> calcined in air at 600°C in the preparation procedure, whereas those of Ir metal detected for the both samples after reduction with H<sub>2</sub>+H<sub>2</sub>O. However, no differences in the diffraction patterns were noticed between Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub>. This suggests that Li does not change the bulk crystal structure of Ir species supported on SiO<sub>2</sub> at the stage of catalyst preparation before the measurement of the catalytic activity.

Then, the X-ray diffraction patterns of the catalysts were recorded after the reaction test performed from 600°C to 200°C. The spectra are shown in Fig.7. In this figure, a clear difference in the patterns can be observed. Namely, Ir/SiO<sub>2</sub> shows mainly the pattern of IrO<sub>2</sub>, while the lines of Ir metal were principally detected for Li/Ir/SiO<sub>2</sub>. These observations indicate that Ir on Ir/SiO<sub>2</sub> is in more oxidized form than that on Li/Ir/SiO<sub>2</sub> after the measurement of the catalytic activity.

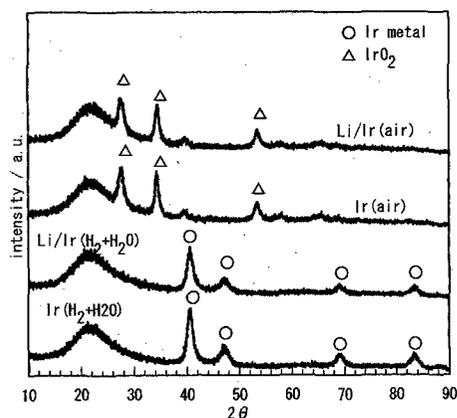


Fig.6 XRD patterns of Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub> during catalyst preparation

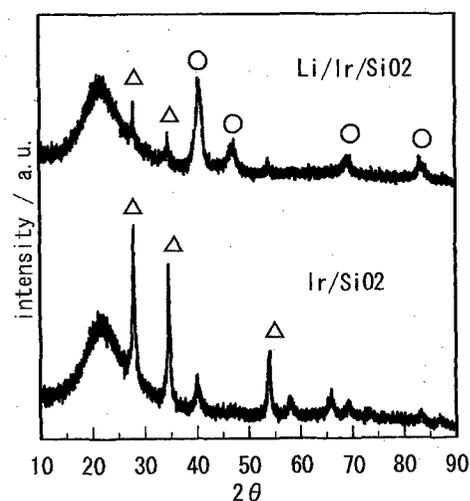


Fig.7 XRD patterns of Ir/SiO<sub>2</sub> and Li/Ir/SiO<sub>2</sub> after use

Consequently, it is probable that Li has an effect to prevent the oxidation of Ir metal during the reaction, which is the active species for NO reduction procedure.

Fig.8 gives the results of catalytic activity evaluation of Ir/SiO<sub>2</sub> under different conditions, that is, at decreasing (from 600°C to 200°C) and increasing reaction temperature (200°C to 600°C) after pre-reduction with H<sub>2</sub>+H<sub>2</sub>O at 600°C. It is evident that at low temperatures around 200°C Ir/SiO<sub>2</sub> showed much higher activity under the latter conditions than under the former conditions. This evidently points out that deactivation of Ir/SiO<sub>2</sub> proceeds in the atmosphere of the reaction gas containing NO, O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O during the activity measurement. Taking the above-described XRD measurement into consideration, it is suggested that the deactivation was caused by oxidation of Ir metal.

Fig.9 shows the catalytic performance of Li/Ir/SiO<sub>2</sub> evaluated under the same conditions of decreasing and increasing reaction temperature. In this case, the difference of catalytic activity between the two conditions is not obvious, suggesting that Li has an effect to prevent the deterioration of the catalyst by retarding Ir oxidation.

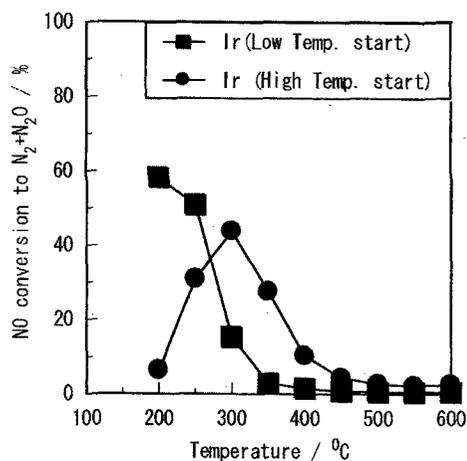


Fig.8 Activity evaluation of Ir/SiO<sub>2</sub> under different conditions of decreasing and increasing temperature

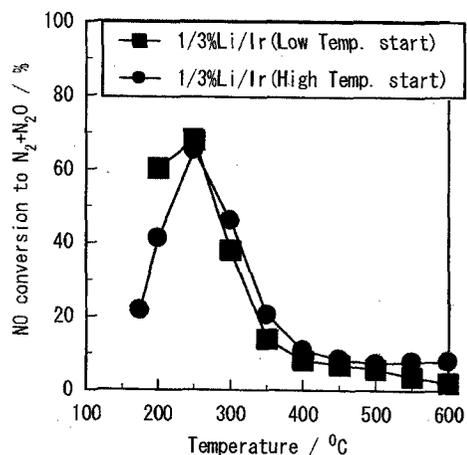


Fig.9 Activity evaluation of Li/Ir/SiO<sub>2</sub> under different conditions of decreasing and increasing temperature

To make sure of the effect of Li against oxidation of Ir, TPO of pre-reduced Li/Ir/SiO<sub>2</sub> with various Li/Ir ratios was performed. Fig.10 indicates the TPO profiles corresponding to O<sub>2</sub> consumption with increasing temperature. The O<sub>2</sub> consumption peak was observed at

502°C for Ir/SiO<sub>2</sub>. As the Li loading was increased, the peak clearly shifted to higher temperature, indicating that the addition of Li makes the oxidation of Ir more difficult. This result agrees quite well with the speculation on the role of Li described above.

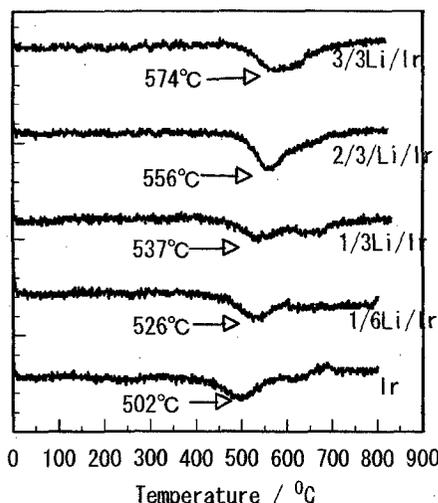


Fig.10 TPO profiles of Li/Ir/SiO<sub>2</sub> with different Li loadings

#### 4. CONCLUSIONS

- (1) The addition of alkali and alkaline earth metals promotes the activity of Ir/SiO<sub>2</sub> for NO reduction with H<sub>2</sub> in the presence of O<sub>2</sub> and SO<sub>2</sub>.
- (2) The promotion effect of alkali metals and alkaline earth metals was in the order of Li > Na > K > none ~ Rb > Cs, and Ba > Sr ~ Ca > none > Mg, respectively.
- (3) The effect of Li addition was observed only at high O<sub>2</sub> concentrations.
- (4) It is concluded that the role of Li is to prevent the deterioration of the catalytic activity by retarding the oxidation of Ir metal on SiO<sub>2</sub>, which is the catalytically active species.

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