Cooperative effect of platinum and alumina for the selective reduction of nitrogen monoxide with propane

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Reduction of nitrogen monoxide with propane in the presence of oxygen proceeded not only on alumina-supported platinum but also on physical mixtures of alumina and silica-supported platinum, both of which are inactive for the selective NO reduction. Spillover, gas phase transfer of some reaction intermediates, or homogeneous propane oxidation seems responsible for the cooperative effect.

Keywords: nitrogen monoxide; selective reduction; propane; platinum; alumina; cooperative effect

1. Introduction

The selective reduction of nitrogen monoxide with hydrocarbons in the presence of oxygen is attracting much attention recently because this reaction is a promising measure for NOx removal in oxygen-rich exhaust gases such as diesel and lean-burn gasoline engine exhaust. Various zeolites [1–4], metal oxides [5,6], and noble metals [7] have been reported to have catalytic activity for this reaction. However, there are still arguments on the catalytic active sites and the reaction mechanism.

We reported that the activity of supported platinum catalysts depends strongly on the support and hydrocarbon species [8]. In the case of NO reduction on Pt/SiO_2, unsaturated and aromatic hydrocarbons serve as excellent reducing agents. However, NO reduction does not proceed with saturated hydrocarbons. On the other hand, Pt/Al_2O_3 is active for NO reduction not only with unsaturated but also with saturated hydrocarbons. This suggests that the activity of Pt/Al_2O_3 for NO reduction with saturated hydrocarbons be attributed to the effect of the alumina support.

In this paper we report that the catalytic activity for NO reduction with propane is generated by cooperation of platinum and alumina and that this cooperative effect is observed even for the physical mixtures of alumina and Pt/SiO_2 for which platinum is not supported on alumina, although the catalytic activity is not sufficiently high for practical applications. Possible reaction mechanisms for this reaction will also be discussed based on the present experimental results.

2. Experimental

The alumina used in this study was obtained from Sumitomo Metal Mining (NK-16280, 250 $m^2 g^{-1}$), and the silica was Fuji-Davison SiO_2 (Cariact-10, 310 $m^2 g^{-1}$). 0.5%Pt/Al_2O_3 was prepared by NE Chemcat with impregnation method using the same alumina (NK-16280) as the support. 0.5%Pt/SiO_2 was prepared by impregnating the silica with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$, followed by reduction at 400°C in H_2.

The catalytic reaction was carried out with a flow reactor by passing a gas mixture over a catalyst. The gas mixture contained 1000 ppm NO or NO_2, 1000 ppm propane, and 10% O_2 diluted in helium. The effluent gas was analyzed by gas chromatography. A Molecular Sieve 5A column was used for the analysis of N_2 and CO, and a Porapak Q column for that of N_2O, CO_2 and hydrocarbons. Transmission electron microscopic analysis was made for catalyst characterization.

3. Results and discussion

Fig. 1 summarizes the activities of SiO_2, Al_2O_3, Pt/SiO_2 and Pt/Al_2O_3 for NO reduction with propane in the presence of 10% O_2. SiO_2 did not show catalytic activity, while Al_2O_3 catalyzed NO reduction to N_2 over 400°C along with oxidation of propane to CO and CO_2. Pt/SiO_2 did not catalyze NO reduction at all but oxidized propane to CO_2 over 250°C. In contrast, Pt/Al_2O_3 showed good activity for NO reduction with formation of CO_2 as the only oxidation product of propane over 250°C. It is noted that N_2O was formed in comparable amounts to N_2 on Pt/Al_2O_3 and that CO was not formed on Pt/SiO_2 and Pt/Al_2O_3.

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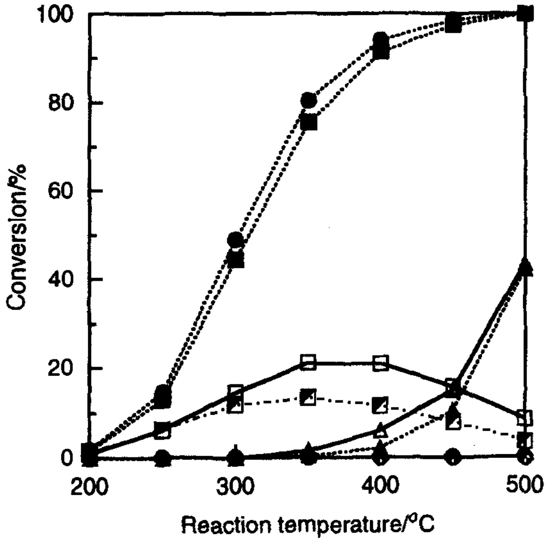

Fig. 1. Activities of SiO_2, Al_2O_3, Pt/SiO_2 and Pt/Al_2O_3 for the selective reduction of NO with propane. NO conversion to N_2: (+) SiO_2, (△) Al_2O_3, (○) Pt/SiO_2, (□) Pt/Al_2O_3; NO conversion to N_2O: (◩) Pt/Al_2O_3; C_3H_8 conversion to COx: (▲) Al_2O_3, (●) Pt/SiO_2, (■) Pt/Al_2O_3. NO = 1000 ppm, C_3H_8 = 1000 ppm, O_2 = 10%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

The catalytic activities of physical mixtures of Pt/SiO_2 and Al_2O_3 are shown in figs. 2a and 2b. In this experiment, the mixtures were prepared by mixing Pt/SiO_2 and Al_2O_3 which had been crushed separately and sieved to desired grain size. When the grain size was large, the activity of the mixture of Pt/SiO_2 and Al_2O_3 for NO reduction was similar to that of Al_2O_3. It is amazing, however, that a deNOx activity similar to that of Pt/Al_2O_3 was observed when the grain size of the mixture was smaller, although the NO conversion was lower than that on Pt/Al_2O_3. The NO reduction activity increased with decreasing grain size. It should be noted from fig. 2b that the conversion of propane to CO_2 was not affected much by the grain size. CO_2 was the only product of propane oxidation and the carbon balance was quite good. No other carbon-containing compounds than propane and CO_2 were detected.

Since the physical mixtures were not prepared by grinding Pt/SiO_2 and Al_2O_3 together in a mortar, mechanochemical effects are not responsible for the cooperative effect of the two catalytic components. To make sure that platinum and alumina did not change during the catalytic activity test, TEM micrographs of the mixture (80–100 mesh) after the activity test were taken. Fig. 3 shows micrographs of an alumina grain and a silica grain in the catalyst mixture, respectively. Apparently, black platinum particles with a diameter of about 10 nm existed not on alumina but on silica. Moreover, it was proved by elemental analysis that the alumina grains did not contain detectable amounts of platinum and that the silica grains were not contaminated by alumina. These results indicate that the physical mixture was still in the form of a mixture of Pt/SiO_2 and Al_2O_3 after the catalytic activity test.

This conclusion was also supported by the experiment shown in fig. 4. In this experiment the activity of a mixture of Pt/SiO_2 (smaller than 100 mesh) and Al_2O_3 (60–80 mesh) was tested. For this mixture, enhancement of the deNOx activity was also observed at about 300–350°C. After the test, the mixture was separated to the original Pt/SiO_2 and Al_2O_3 grains by sieving. The activity of the separated Pt/SiO_2 and Al_2O_3 was very close to that of the fresh catalyst samples, as shown in fig. 4. Slight decrease in the activity can be ascribed to loss of the sample during the sieving procedure.

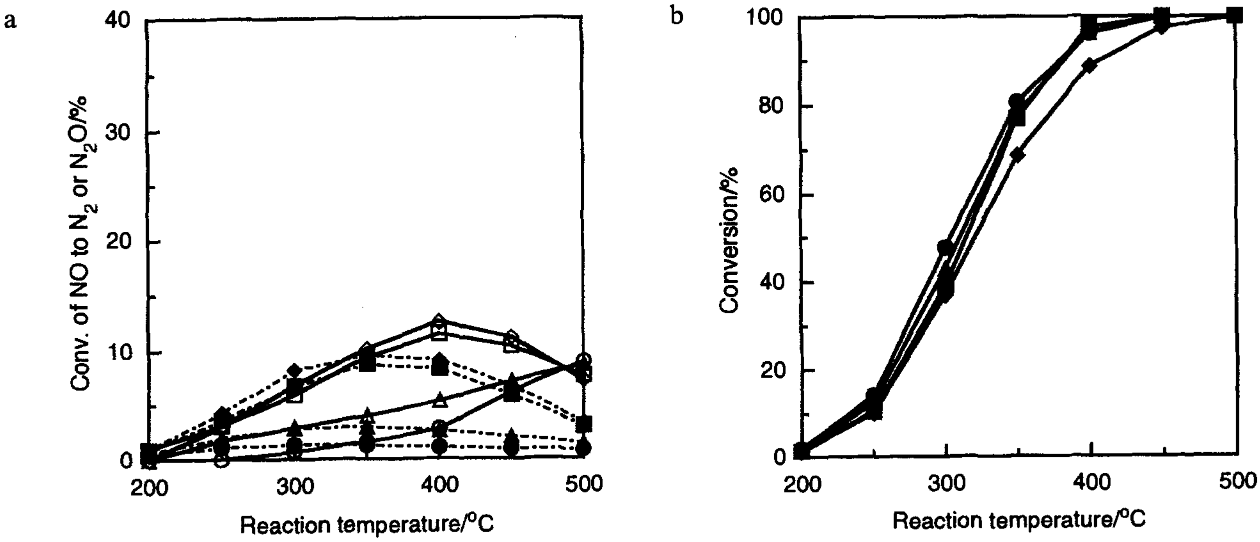

Fig. 2. (a) Conversion of NO in the selective reduction of NO with propane over physical mixtures of Pt/SiO_2 and Al_2O_3. NO conversion to N_2: (○) 20–32 mesh, (△) 42–60 mesh, (□) 80–100 mesh, (◇) 100– mesh; NO conversion to N_2O: (●) 20–32 mesh, (▲) 42–60 mesh, (■) 80–100 mesh, (◆) 100– mesh. NO = 1000 ppm, C_3H_8 = 1000 pp, O_2 = 10%, catalyst weight = 0.2 g Pt/SiO_2 + 0.2 g Al_2O_3, gas flow rate = 66 cm^3 min^{-1}. (b) Conversion of propane in the selective reduction of NO with propane over physical mixtures of Pt/SiO_2 and Al_2O_3. C_3H_8 conversion to CO_2: (●) 20–32 mesh, (▲) 42–60 mesh, (■) 80–100 mesh, (◆) 100– mesh. The reaction conditions are the same as for (a).

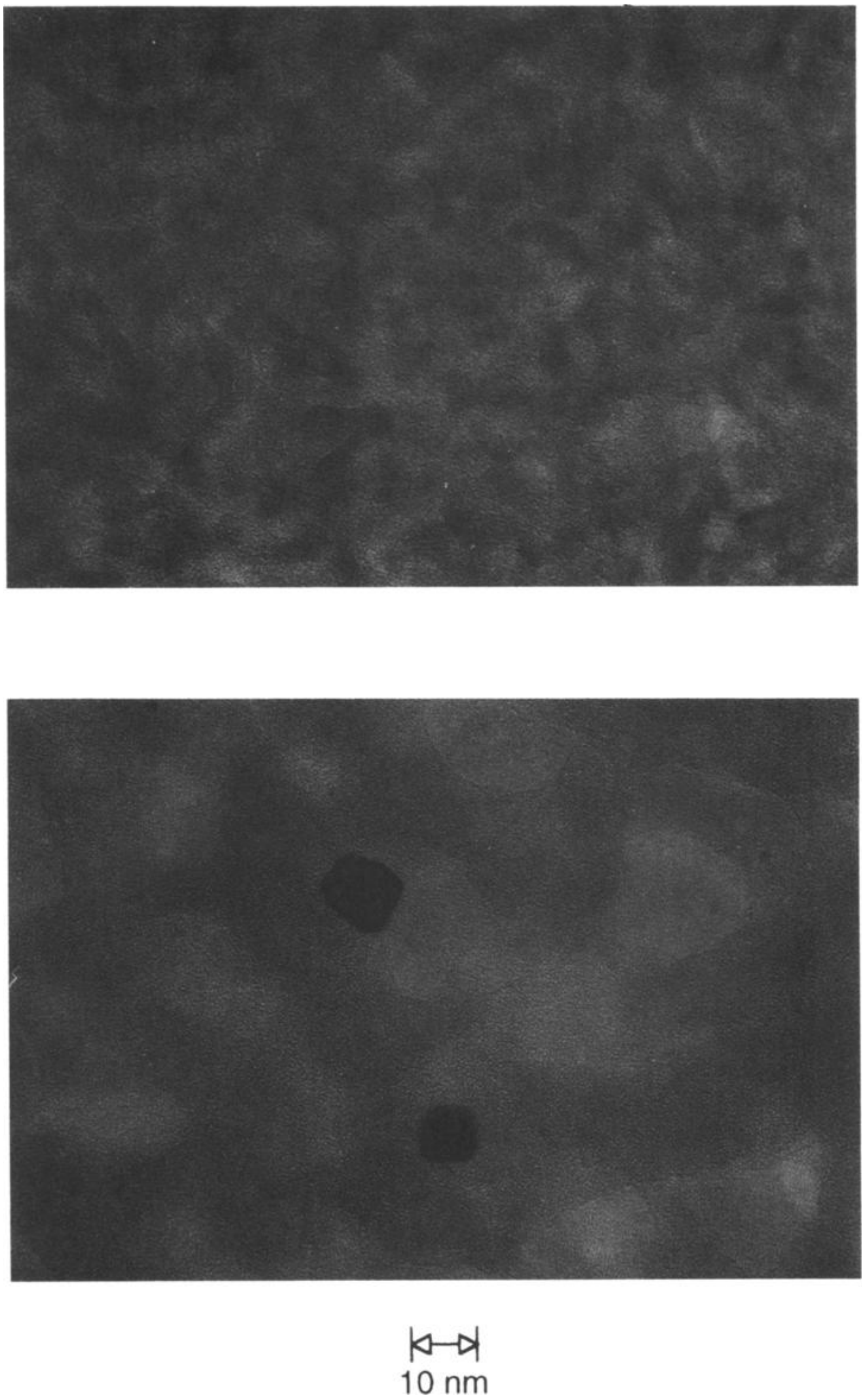

Fig. 3. TEM micrograph of the surface of an alumina grain (upper) and a silica grain (down) in the mixture of Pt/SiO_2 and Al_2O_3 after the activity test.

Consequently, it can be concluded that NO reduction results from some kind of cooperative effect between Pt/SiO_2 and Al_2O_3 because it is not plausible that only physical mixing brings platinum into contact with alumina. It was also confirmed experimentally that the activity of Pt/SiO_2 or Al_2O_3 was not affected by changing their grain size.

The activities of Pt/SiO_2 and Al_2O_3 for the reduction of NO_2 instead of NO were examined next. As shown in fig. 5, Pt/Al_2O_3 and Pt/SiO_2 gave almost the same

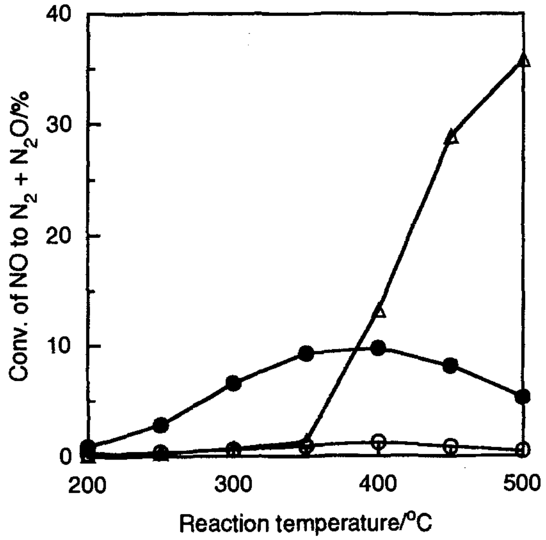

Fig. 4. Activity of Pt/SiO$_2$ and Al$_2$O$_3$ separated from a physical mixture. (●) Mixture of Pt/SiO$_2$ and Al$_2$O$_3$, (○) Pt/SiO$_2$, (△) Al$_2$O$_3$. The reaction conditions are the same as for fig. 2.

results for both NO reduction and NO$_2$ reduction. For example, NO$_2$ was not reduced to N$_2$ or N$_2$O on Pt/SiO$_2$. On Al$_2$O$_3$, however, the reduction of NO$_2$ took place more easily than that of NO. We already reported this fact and assumed that NO$_2$ be a reaction intermediate over alumina-catalyzed NO reduction [9]. Accordingly, one hypothesis may be that Pt/SiO$_2$ promotes oxidation of NO to NO$_2$ and that N$_2$ is formed through the reaction of NO$_2$ with propane on Al$_2$O$_3$. Actually Pt/SiO$_2$ is an effective catalyst for NO oxidation. However, it can be seen from figs. 2a and 5 that the formation of N$_2$ at 300 and 350°C from NO reduction on Pt/SiO$_2$–Al$_2$O$_3$ physical mixtures is clearly higher than that from NO$_2$ reduction on alumina. Moreover, N$_2$O was not formed as a reduction product of NO$_2$ on alumina. Therefore the above-mentioned hypothesis can be ruled out. Yokoyama and Misono [10] reported recently that mixing Mn$_2$O$_3$ to Ce-ZSM-5 promoted NO reduction activity at lower temperatures. Similar results were also obtained for mixtures of Au/Al$_2$O$_3$ and Mn$_2$O$_3$ [11]. They concluded that the effects are due to the promotion of NO oxidation to NO$_2$ by Mn$_2$O$_3$. The present cooperative effect, however, cannot be explained only by contribution of NO oxidation reaction on Pt/SiO$_2$.

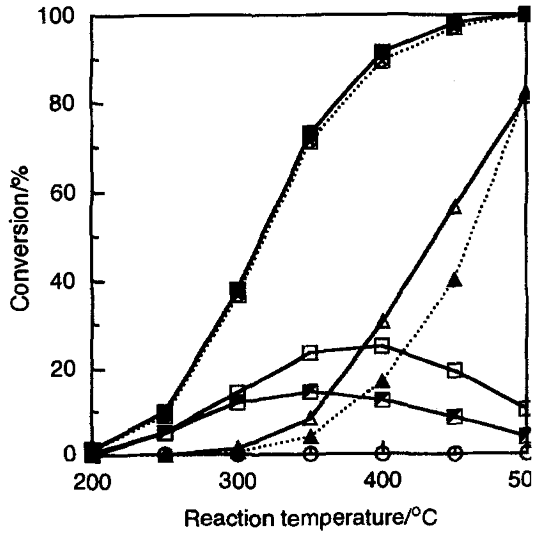

Fig. 5. Activities of Al$_2$O$_3$, Pt/SiO$_2$ and Pt/Al$_2$O$_3$ for the selective reduction of NO$_2$ with propane. NO conversion to N$_2$: (△) Al$_2$O$_3$, (○) Pt/SiO$_2$, (□) Pt/Al$_2$O$_3$; NO conversion to N$_2$O: (▨) Pt/Al$_2$O$_3$; C$_3$H$_8$ conversion to COx: (▲) Al$_2$O$_3$, (●) Pt/SiO$_2$, (■) Pt/Al$_2$O$_3$. NO$_2$ = 1000 ppm, C$_3$H$_8$ = 1000 ppm, O$_2$ = 10%, catalyst weight = 0.2 g, gas flow rate = 66 cm^3 min^{-1}.

A lot of mechanisms have been proposed so far concerning the selective NO reduction with hydrocarbons in the presence of an excess of oxygen. In general, they can be classified into the following two suggestions.

(a) N$_2$ is formed through NO decomposition based on a redox mechanism, while the hydrocarbon and/or oxygen regenerate or maintain the surface active sites [12,13]. The hydrocarbon may remove the surface oxygen poisoning the active sites. Oxygen may prevent the over-reduction of the active sites [14].

(b) N$_2$ is formed from a series of reaction steps between the hydrocarbon and NO possibly via a partially oxidized hydrocarbon [15–17] or NO$_2$ [9,18,19], for the formation of which oxygen is necessary. Nitrogen-containing intermediates such as isocyanates [20] and organic nitro compounds [21] have been proposed as reaction intermediates leading to the formation of N$_2$. An active carbonaceous material, which is formed from the hydrocarbon, was also proposed as responsible for the formation of N$_2$ [17,22]. Oxygen may prevent the deposition of carbonaceous deposits which would cover the active sites [23].

In this study, it is clear that the NO reduction proceeds by cooperation of Pt/SiO$_2$ and Al$_2$O$_3$. Since propane conversion to CO$_2$ on Pt/SiO$_2$ was little influenced by mixing with Al$_2$O$_3$, it is suggested that the initial rate-determining step be the oxidation of propane by O$_2$ on platinum surface. The following reaction steps leading to the formation of N$_2$ and N$_2$O are not clear at the moment but the presence of alumina definitely participates in the reduction of NO. Therefore, mechanism (a) is unlikely because NO reduction should proceed on single catalytically active sites, while N$_2$ is formed by cooperation of the two catalytic species in the present case.

In the case of mechanism (b), spillover or gas phase transfer of some reaction intermediates from platinum to alumina or vice versa might explain the cooperative effect. Since no other carbon-containing compounds than CO$_2$ and propane were detected in the gas phase, the intermediates should not be so stable. The effect of grain size can be explained by the short life of the intermediates. Possible candidates are partially-oxidized hydrocarbons on platinum or activated hydrocarbons on alumina. Nishizaka and Misono [24,25] reported recently that the presence of both palladium and acid site of H-ZSM-5 is necessary for the selective reduction of NO with methane to take place, although the catalyst was not a physical mixture. The present study may be related to their results. In any case it is natural to think that the activation of NO, oxygen and the hydrocarbon is needed for the selective reduction [26]. Alumina and platinum may act as the active species for activation of the hydrocarbon, NO and oxygen.

An attractive mechanism was proposed recently by Lukianov et al. for NO reduction on Co-ZSM-5 and H-ZSM-5 [27]. In their mechanism, the combustion of the hydrocarbon proceeds homogeneously initiated by radical formation from NO_2 and the catalyst serves to retain a reaction intermediate such as organic nitro compounds which could react with NO or NO_2 to form a N–N bond. The cooperative effect in the present study can be explained by assuming a homogeneous propane combustion in the gas phase. The homogeneous combustion may be initiated on platinum and partially oxidized hydrocarbons can reach through gas phase to the surface of alumina, where NO reduction occurs. However, NO_2 does not seem to participate in propane combustion as reported by Lukianov et al. because the propane conversion to CO_2 for the NO–C_3H_8–O_2 reaction was found almost the same as that for the C_3H_8–O_2 reaction. Further studies are necessary to elucidate the actual mechanism of the cooperative effect of Pt/SiO_2 and Al_2O_3.

4. Summary

The selective reduction of NO with propane in the presence of oxygen was investigated over Pt/SiO_2, Pt/Al_2O_3, Al_2O_3, and physical mixtures of Pt/SiO_2 and Al_2O_3. Although Pt/SiO_2 did not show any deNOx activity, Pt/Al_2O_3 was active for NO reduction to N_2 and N_2O at about 300–400°C. Al_2O_3 catalyzed NO reduction to N_2 only above 400°C without giving N_2O. It was found that the deNOx activity similar to Pt/Al_2O_3 was observed for physical mixtures of Pt/SiO_2 and Al_2O_3, especially when the grain size was small. Since the state of the physical mixture did not change during the activity test, it was concluded that the reduction of NO to N_2 and N_2O results from successive reaction steps over platinum and alumina. Catalytic activity tests using NO_2 revealed that the cooperative effect cannot be explained by promotion of NO oxidation to NO_2 on Pt/SiO_2. Spillover, gas phase transfer of certain reaction intermediates from platinum to alumina or vice versa or homogeneous oxidation reaction could account for the effect.

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