Selective Catalytic Reduction of NO in Diesel Exhaust over Anodic Alumina Catalyst

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A series of Cu-Mn-Ce/Al₂O₃ anodic alumina catalysts synthesized using the multi-impregnation method were employed to investigate the selective reduction of NO with C₃H₆ in the presence of excess O₂. The presence of Cu additive greatly promoted the low-temperature de-NO_x activity. A moderate loading of copper gave the most promising NO_x conversion. In contrast, no promotional effect on low-temperature de-NO_x activity was found when Mn was added to the alumina support. Although the Mn-supported catalyst exhibited a higher activity for the oxidation of NO to NO₂, the addition of Mn to the Cu-Ce/Al₂O₃ catalyst had no positive effect on NO_x reduction, due to the wasteful consumption of propene. The de-NO_x activity of the Cu-Ce/Al₂O₃ catalyst was maintained at a relatively high level, even in the presence of excess SO₂ (500 ppm) and H₂O (10 vol%). Furthermore, the presence of SO₂ was observed to greatly promote NO_x reduction at 723 K.

Key Words : Anodic Alumina Catalyst, Selective Catalytic Reduction, NO_x Removal, Copper, Manganese

1. Introduction

The selective catalytic reduction of NO with hydrocarbons as reducing agents (SCR-HC of NO) has received much attention as a possible means of controlling the emissions from diesel vehicles in which engines operate under oxygen-rich conditions. Most of the reports published so far are related to zeolite catalysts such as Cu-ZSM-5, Fe-ZSM-5 and Pt/H-ZSM-5^{1)~3)}. Though zeolite-based catalysts have been reported to be highly active for the present reaction, their poor hydrothermal properties, diffusion limitations and narrow operating windows make them unsuitable from a practical point of view.

Metal-supported oxide catalysts have become the focus of recent research on the SCR-HC of NO due to their good thermal and hydrothermal stabilities and wide operating windows. γ -alumina appears to be one of the most active single metal oxides, and its de-NO_x activity can be further promoted by a wide range of metal and metal oxides such as Pt, Co, Ag and Cu. Cu has been identified as one of the most promising elements for the SCR-HC of NO^{4)~7)}. In our present study, Cu was employed as the active metal and γ -alumina was used as the support. Mn was selected as a sub-metal to promote the conversion of NO to NO₂, which is known to be one of the key steps^{8)~12)}.

In this study, anodization of aluminum was used to prepare the γ -alumina support. Porous alumina film can be formed on the surface of aluminum plate by anodization. Subsequently, hot water treatment and calcination transform the amorphous anodic alumina

film into γ -alumina, and greatly increase its surface area¹³⁾. The γ -alumina film prepared by this technology has a surface area (ca. 140 m²·(g-Al₂O₃)⁻¹) comparable to some commercial bead alumina catalysts. However, our previous research showed that a catalytic reactor prepared with the anodic alumina catalyst has a higher heat transfer coefficient than a traditional packed alumina catalytic reactor¹⁴⁾. In fact, the bead alumina catalyst has been rejected from catalyst support markets for auto exhaust control since the 1980's, due to its poor thermal conductivity and high pressure drop. From a practical point of view, alumina must be highly dispersed on a carrier. The carrier should have a high loading area and favorable thermal conductivity, and allow a low pressure drop, as observed in the honeycomb-type ceramic carrier. In our anodic alumina catalyst, the alumina film comes from the surface of aluminum, and part of the aluminum (ca. 100 μ m) remains in the interlayer of the catalyst. For this reason, an additional carrier is unnecessary in loading alumina. Comparison with commercial honeycomb-type ceramic catalysts (e.g. DASH-20 M supplied by Japan Engelhard Inc., surface area : 13 m²·(g-Al₂O₃)⁻¹) shows that the anodic alumina catalyst has a sufficiently large surface area. Furthermore, since anodization is conducted in aqueous solution, an aluminum material with a complex structure such as honeycomb, mesh and serrated honeycomb can easily be prepared into an alumina support that allows a relatively low pressure drop^{13)~16)}. Therefore, application of the anodic alumina support in auto exhaust control is a promis-

ing area for further study.

In this paper, we report our results on the investigation into the activity of anodic alumina catalyst for the SCR-NO with C₃H₆.

2. Experimental

A commercial aluminum plate (JIS A 1050, thickness 0.3 mm) was pre-treated in 20 wt% of sodium hydroxide for 3 min and 30 wt% of nitric acid for 1 min, and then rinsed with deionized water. The pre-treated aluminum plate was anodized in 4.0 wt% of oxalic acid for 16 h at an electric current density of 50 A·m⁻² and a temperature of 293 K, to form porous alumina film (ca. 100 μm). The plate was then washed, dried naturally, and calcined at 623 K to remove residual oxalic acid. Subsequently, hot water treatment (HWT) in deionized water at 353 K was conducted for 1 h. The resulting plate was calcined in air at 773 K for 3 h to obtain the γ-alumina support.

Cu and Mn were selected as an active metal and a sub-metal, for the reasons discussed in section 1. In addition, Ce was used to improve the thermal stability of the catalyst, especially at high temperatures^{17), 18)}. The co-impregnation method was employed to synthesize the Cu, Mn and Ce supported alumina catalysts. In this case, the anodic γ-alumina support was impregnated by using an aqueous solution containing the required amounts of Cu(NO₃)₂·3H₂O, Mn(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O, for 1 h under ambient conditions. The resulting plate was then dried naturally for 4 h, and calcined in air at 773 K for 3 h. The impregnation and the calcination were repeated 5 times, to enhance metal loading. During impregnation, pH adjustment of the impregnation solution was not carried out, and the aqueous solution was used directly to load the metals.

BET specific surface area and pore radius were measured by a nitrogen adsorption method (COULTER SA 3100). X-ray powder diffraction (XRD) analyses were performed on a SHIMADZU

XRD-6000, using Cu Kα radiation. The metal contents were measured by atomic absorption spectrometry (SHIMADZU AA-680), and they are reported in this paper based on the apparent surface area of the catalyst (both sides of the plate-type catalyst, i.e. g·m⁻²). However, it should be noted that measurement of Ce loading using this technique is difficult, due to the relatively low Ce content, so Ce content is not given. Unless otherwise stated, 0.1 mol·L⁻¹ Ce was simultaneously added into the impregnation solution. Hereafter, the synthesized catalysts are referred to as Cu(x)-Ce(0.1)/Al₂O₃, Mn(y)-Ce(0.1)/Al₂O₃ and Cu(x)-Mn(y)-Ce(0.1)/Al₂O₃, where x and y are the metal-ion concentrations (mol·L⁻¹) of Cu and Mn in the impregnation solution, respectively.

A plug flow integrated reactor (i.d. 15 mm) was used to test the de-NO_x activity of each synthesized catalyst. The plate-type catalyst was cut into small pieces (ca. 5 mm²) and packed in the reactor, using quartz sand for dilution with a loading density of 0.4 cm²-catalyst·(g-quartz sand)⁻¹. Both inlet and outlet stream mixtures were analyzed. Gas chromatographs were used to analyze C₃H₆ (FID), O₂, N₂ and CO (TCD). NO_x (NO and NO₂) was measured with a chemiluminescent NO_x analyzer (HORIBA PG-235 gas analyzer). An infrared gas analyzer (SHIMADZU CGT-7000) was used to measure the CO₂ formed. A GC-MS (SHIMADZU GCMass-QP 5050) equipped with a GS-Q column was utilized to analyze the production of N₂O. The amount of SO₂ was measured using an infrared SO₂ gas analyzer (SHIMADZU SOA-7000). A micro piston pump was used to introduce H₂O into a vaporizer, and the amount of added H₂O was measured by a balance. The reaction feed-stream was prepared by mixing certified analyzed model gases (supplied by TOEI CHEM.), with helium as the carrier gas. The total gas flow rate was set at 9.0 L·h⁻¹ (F/W = 37.5 L·(g-catalyst)⁻¹·h⁻¹).

The results obtained were evaluated in terms of NO_x conversion, C₃H₆ conversion, N₂ selectivity and CO

Table 1 Preparation conditions and characteristics of the anodic alumina catalysts.

Concentration of metal-ion		Metal loading		BET surface area [m ² ·(g-Al ₂ O ₃) ⁻¹]	Pore radius [nm]
Cu [mol·L ⁻¹]	Mn [mol·L ⁻¹]	Cu [g·m ⁻²]	Mn [g·m ⁻²]		
—	—	—	—	138.7	2.88
0.017	—	4.84	—	90.1	4.11
0.033	—	7.68	—	89.3	4.22
0.067	—	8.90	—	97.8	4.42
0.133	—	10.7	—	97.3	4.39
0.267	—	12.1	—	96.1	4.35
0.400	—	12.6	—	95.9	4.30
—	0.25	—	3.23	76.5	3.54
—	0.50	—	6.41	78.3	3.69
—	1.00	—	7.02	84.7	3.74
—	1.50	—	7.05	81.5	3.71
—	2.00	—	6.99	82.7	3.80
0.033	0.10	7.61	0.97	83.2	3.64
0.033	0.50	7.54	5.51	79.9	3.68

selectivity. N_2 selectivity was defined as $: 2 \times N_2 \text{ produced} / (NO_x \text{ inlet} - NO_x \text{ outlet}) \times 100\%$, and CO selectivity was expressed as $: CO_{\text{produced}} / (3 \times (C_3H_6 \text{ inlet} - C_3H_6 \text{ outlet})) \times 100\%$ (NO_x , N_2 , CO and C_3H_6 : molar flow rate).

3. Results and Discussion

Using the anodic alumina support, a series of Cu-Mn-Ce/ Al_2O_3 catalysts were prepared by varying the Cu and Mn concentrations in the impregnation solution. The characteristics of these catalysts are presented in Table 1. An anodic alumina support used as a reference catalyst is also listed in Table 1. Comparison of the alumina support with the metal-supported alumina catalysts shows a decrease in BET specific surface area and an increase in pore radius. Dissolution of the alumina film in the acidic impregnation solution is considered to be responsible for this change. Cu and Mn loadings are gradually enhanced as the metal-ion concentrations are increased. How-

ever, a limitation to metal loading is observed when the impregnation concentration exceeds a specific value, which is determined by the adsorption equilibrium of metal ions and the diffusion resistance in micropores under the present conditions. Another possible reason for this could be the dynamic balance between the metal adsorption and the dissolution of the alumina film.

Figure 1 shows the catalytic activities of different alumina catalysts for (a) NO_x conversion, (b) C_3H_6 conversion, (c) N_2 selectivity and (d) CO selectivity. It should be noted that the catalytic activity values associated with a metal loading of zero were achieved over the alumina support. In Fig. 1(a), the alumina support gives maximal NO_x conversion at 823 K. Nevertheless, compared with the alumina support, the Cu-Ce/ Al_2O_3 catalyst exhibits a higher de- NO_x activity when the temperature is less than 673 K. For example, at 623 K, the $4.84 \text{ g} \cdot \text{m}^{-2}$ Cu additive greatly increases NO_x conversion, from 8% to 28%. This

Fig. 1 Catalytic activities of Cu-Ce/ Al_2O_3 and Mn-Ce/ Al_2O_3 as a function of metal (Cu or Mn) loading.

(a) NO_x conversion ; (b) C_3H_6 conversion ; (c) N_2 selectivity ; (d) CO selectivity (O_2 15.0 vol%, C_3H_6 0.5 vol%, NO 1000 ppm)

proves that Cu exerts a significant influence on the SCR-HC of NO. In addition, the addition of Cu is observed to have different effects on reducing NO_x, depending on temperature. At low temperatures (573 K and 623 K), NO_x conversion always increases with an increased Cu loading. In contrast, at 773 K, an increase in copper loading gradually decreases NO_x conversion. At an intermediate temperature of 673 K, NO_x conversion is firstly promoted from 36% to 43% with an increase in copper loading from 4.8 to 10.7 g·m⁻², but further increases in copper loading reduce NO_x conversion. This result at 673 K indicates that a moderate Cu loading gives the most promising NO_x conversion. This bell-type plot at 673 K is in agreement with the work reported by Amin *et al.*⁶⁾ and Shimizu *et al.*¹⁹⁾, which demonstrated that intermediate loading of an active metal always gave the most promising result, regardless of the catalyst support. In the case of the Mn-Ce/Al₂O₃ catalyst, however, the promotional effect on low-temperature de-NO_x activity is not found.

As shown in Fig. 1(b), the presence of metal additives greatly improves the propene oxidation. In the case of the Cu-Ce/Al₂O₃ catalyst, comparison of Fig. 1(a) with Fig. 1(b) shows that the NO_x reduction is coincident with the C₃H₆ oxidation. That is, NO_x conversion is increased as propene is effectively oxidized (or activated), but once C₃H₆ conversion approaches 100%, NO_x reduction is depressed. At low temperatures, propene activation improves with increasing Cu loading, which is one main reason for the increase in NO_x conversion. On the other hand, at high temperatures, an increase in Cu loading overly accelerates propene oxidation by oxygen rather than NO_x, which results in a lack of propene available for NO_x reduction.

The formation of a small amount of N₂O accompanying the NO_x reduction was detected, which makes N₂ selectivity less than 100% (Fig. 1(c)). N₂ selectivity gradually decreases with increasing Cu (or Mn) loading. In comparison with Mn-Ce/Al₂O₃, Cu-Ce/Al₂O₃ exhibits promising N₂ selectivity.

CO selectivity is presented in Fig. 1(d). The undesirable production of CO, as a by-product of the partial oxidation of propene, obviously decreases with increasing metal loading. CO production is almost negligible, especially over the Cu-Ce/Al₂O₃ catalyst. Although the alumina support exhibits maximal NO_x conversion at 823 K, excess production of CO is observed simultaneously. The higher optimal temperature (823 K) and excess production of CO are two major disadvantages that limit the application of the alumina support as a denitration catalyst. In addition, they indicate that the poor activation of propene by O₂ (or NO_x), which is known to be one of the key steps of the SCR-HC of NO^{8)~10)}, is responsible for the low activity of the alumina support at low temperatures.

Although Mn-Ce/Al₂O₃ exhibits poor de-NO_x activity at any temperature (Fig. 1(a)), the Mn additive un-

doubtedly improves propene oxidation (Fig. 1(b)). This result indicates that a Mn-supported catalyst has favorable propene oxidation ability, but insufficient selectivity for NO_x reduction.

In regard to the low-temperature de-NO_x activity, the effect of a metal additive on the oxidation of NO to NO₂ must be taken into account. The beneficial effect of using NO₂ instead of NO as a starting NO_x molecule has already been extensively reported for the SCR-HC over metal-promoted γ -alumina catalysts^{8)~10), 20)}. Figure 2 shows the activities of different alumina catalysts for the oxidation of NO to NO₂ (without any reducing agent). The dotted line represents the thermodynamic limitation of NO₂ yield associated with the following reaction :

No product other than NO₂ was observed in the outlet stream. In a blank experiment, a NO₂ yield of 6% was detected due to NO oxidation in the line pipes. Compared with the result for the blank experiment, the similar NO₂ yield achieved over the alumina support shows that the support has a low reactivity for NO oxidation. The addition of Cu substantially enhances NO₂ yield, and this promotional effect becomes more intense as the Cu loading increases. Accordingly, at low temperatures, the presence of Cu is considered to promote both the propene activation and the NO oxidation. At high temperatures, however, NO₂ yield is not further increased by a higher Cu loading, due to the equilibrium limitation. Moreover, the oxidation of C₃H₆ by O₂ increasingly prevails over the C₃H₆ + NO_x reaction with increasing Cu loading, and decreases NO_x conversion. In Fig. 2, Mn-Ce/Al₂O₃ shows a strong reactivity for the oxidation of NO to NO₂, and this oxidation ability is superior to that of Cu-Ce/Al₂O₃. For this reason, we added Mn to Cu-

Fig. 2 Oxidation of NO to NO₂ achieved over different catalysts.

(O₂ 5.0 vol%, NO 1000 ppm)

Ce/Al₂O₃ to improve the NO oxidation. The characteristics of the Cu-Mn-Ce/Al₂O₃ catalysts are also presented in Table 1. As shown in Fig. 2, the addition of Mn to Cu-Ce/Al₂O₃ significantly improves the NO oxidation activity of Cu-Ce/Al₂O₃.

Figure 3 shows (a) NO_x conversion, and (b) C₃H₆ conversion achieved over Mn(0.5)-Ce(0.1)/Al₂O₃, Cu(0.033)-Ce(0.1)/Al₂O₃ and Cu(0.033)-Mn(0.1 or 0.5)-Ce(0.1)/Al₂O₃. The addition of Mn to Cu(0.033)-Ce(0.1)/Al₂O₃ slightly improves NO_x reduction at low temperatures, but significantly decreases NO_x conversion at high temperatures. Fig. 3(b) shows a large increment in C₃H₆ conversion caused by Mn addition. As discussed for Fig. 2, the addition of Mn to Cu-Ce/Al₂O₃ effectively improves the NO oxidation, which is considered to be one of the main reasons for the increase in NO_x conversion at low temperatures. The improved propene activation is the other factor. At high temperatures, the promotional effect of Mn additive on the oxidation of NO is limited by the thermodynamic equilibrium. Furthermore, the addition of Mn accelerates the wasteful consumption of C₃H₆ by O₂ too much, and directly results in a decrease in NO_x conversion. Kim *et al.*⁵⁾ reported a similar result, that the addition of Mn or La to a copper-supported aluminate catalyst had no positive effect on NO reduction with C₃H₆. They proposed that the Mn and La additives did not penetrate well into the alumina structure due to the low spinel formation rates of Mn and La, and surface La and Mn accelerated the O₂+C₃H₆ reaction.

Figure 4 shows the XRD patterns of different anodic alumina catalysts. The broad diffraction lines of low intensity at $2\theta=37.6, 39.4, 45.9$ and 66.8 associated with the alumina support indicate the presence of crystalline γ -alumina. All samples exhibited the same pattern of diffraction peaks as the parent γ -alumina. This result demonstrates that the impregnation with Cu, Mn and Ce does not destroy the original framework of the alumina support. In Figs. 4(b), (c) and (d), there are no diffraction lines attrib-

utable to crystalline bulk oxide phases of the metals supported. It is supposed that the relatively low metal loading (< 4 wt%, based on the weight of alumina film) makes the detection by wide-angle XRD difficult.

Figure 5 shows the results of the stability test in the presence or absence of SO₂ (500 ppm) and H₂O (10 vol%) achieved over Cu(0.033)-Ce(0.1)/Al₂O₃ at 723 K. NO_x and C₃H₆ conversions are decreased when 10 vol% H₂O is present in the feedstream, due to the competitive adsorption of water vapor and reactants on active sites. This is almost reversible when H₂O is switched off. The small difference remaining for NO_x conversion is related to the effect of vapor on the alumina support, similar to the hydration of alumina. Interestingly, when 500 ppm SO₂ is added into the feedstream, a dramatic increase in NO_x conversion (from 39% to 50%) is observed, accompanied by an obvious increase in CO selectivity and a small drop in propene conversion. Furthermore, this promotional effect on

Fig. 4 X-ray diffraction patterns of different catalysts. (a) Alumina support; (b) Cu(0.033)-Mn(0.5)-Ce(0.1)/Al₂O₃; (c) Cu(0.033)-Ce(0.1)/Al₂O₃; (d) Mn(0.5)-Ce(0.1)/Al₂O₃

Fig. 3 Catalytic activities of Cu-Ce/Al₂O₃, Mn-Ce/Al₂O₃ and Cu-Mn-Ce/Al₂O₃. (a) NO_x Conversion, (b) C₃H₆ Conversion (O₂ 15.0 vol%, C₃H₆ 0.5 vol%, NO 1000 ppm)

Fig. 5 Effect of H₂O and SO₂ over Cu(0.033)-Ce(0.1)/Al₂O₃ upon step-feed and shut-off of SO₂ and H₂O at 723 K.

(O₂ 15.0 vol%, C₃H₆ 0.5 vol%, NO 1000 ppm, SO₂ 0 or 500 ppm, H₂O 0 or 10 vol%)

NO_x reduction becomes more dramatic when H₂O and SO₂ are introduced into the feedstream simultaneously. The presence of SO₂ is considered to impede the wasteful consumption of C₃H₆ by O₂, and make more C₃H₆ available for the NO_x reduction. However, it should be noted that excess SO₂ might also impede propene activation. The addition of vapor is supposed to dilute SO₂ and lessen the SO₂ inhibition of propene activation. During aging in H₂O and SO₂ for 10 h, no significant decay in the de-NO_x activity was observed. We do not yet have sufficient knowledge to explain the promotional effect of SO₂ on NO_x reduction over the Cu-Ce/Al₂O₃ alumina catalyst. The formation of sulfate-like species may be one possibility. A more detailed study is now in progress.

According to the aforementioned results, the Cu-Ce/Al₂O₃ anodic alumina catalyst shows favorable de-NO_x activity even in the presence of excess H₂O and SO₂. This is very promising for further development of the Cu-Ce/Al₂O₃ catalyst as a denitration catalyst for the SCR-HC of NO_x in diesel engine exhaust. With regard to the application of the Cu-Ce/Al₂O₃ catalyst for NO_x removal, the coexistence of toxic particulate matter (PM) originating from incomplete combustion in diesel engine exhaust cannot be neglected. In our study, in cooperation with Lead Industry Company Ltd., we designed a novel catalytic purification system for the simultaneous removal of NO_x and PM (shown in Fig. 6). Controlled amounts of air and fuel are introduced into the PM combustion chamber to burn off PM over a Pt-supported anodic alumina catalyst⁽²¹⁾. The residual fuel in the outlet stream is used as reducing agent to add into the NO_x purification chamber for NO_x removal over the Cu-Ce/Al₂O₃ alumina catalyst. Temperature control of the NO_x purification chamber can prevent a mismatch between the temperature of engine exhaust and the optimal operating window of the denitration catalyst. Moreover, the availability of appropriate concentrations of reductants by the adjustment of the air/fuel ratio is considered the most valuable aspect. However, it is impractical to direct-

Fig. 6 Catalytic purification reactor for removal of PM and NO_x.

ly introduce propene for the feed of the PM combustion chamber for removal of PM and NO_x. Research on utilizing fuel oil (e.g. kerosene) instead of propene is now in progress. In addition, due to the low melting point of the aluminum interlayer, overheating may result in the destruction of the aluminum-containing composites. Hence, the thermal stability of the anodic alumina catalyst must be further improved. Recently, a clad aluminum material, in which an Fe/Cr alloy interlayer is clad by an aluminum film of 40 μm, has been adopted as a base material to prepare a clad anodic alumina catalyst. Research shows that the clad alumina catalyst is unchanged at a higher temperature (until ca. 1073 K). A more detailed study is now in progress.

4. Conclusions

A series of Cu-Mn-Ce/Al₂O₃ anodic alumina catalysts synthesized using the multi-impregnation method were employed to investigate the selective reduction of NO with C₃H₆ in the presence of excess oxygen.

The presence of Cu additive greatly promoted the low-temperature NO_x removal activity. A moderate loading of copper gave the most promising NO_x conversion. In contrast, no promotional effect on low-temperature de-NO_x activity was found when Mn was added to the alumina support. Although the Mn-supported catalyst exhibited a higher activity for the oxidation of NO to NO₂, the addition of Mn to the Cu-Ce/Al₂O₃ catalyst had no positive effect on NO_x reduction, due to the wasteful consumption of propene. The de-NO_x activity of the Cu-Ce/Al₂O₃ catalyst was maintained at a relatively high level, even in the presence of excess SO₂ (500 ppm) and H₂O (10 vol%). Furthermore, the presence of SO₂ was observed to dramatically promote NO_x reduction at 723 K.

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References

- 1) M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa ; *J. Phys. Chem.*, 95, 3727 (1991)
- 2) V. Pitchon and A. Fritz ; *Appl. Catal. B : Environmental*, 13, 1 (1997)

- 3) D. Michel, F. Jennifer and F. Robert ; *Appl. catal. A* : General, 188, 219 (1999)
 - 4) P. Carniti, A. Gervasini, V. Modica and N. Ravasio ; *Appl. Catal. B* : Environmental, 28, 175 (2000)
 - 5) T. W. Kim, M. Kang, H. L. Koh and K. L. Kim ; *Journal of Chemical Engineering of Japan*, 34, 221 (2001)
 - 6) N. A. S. Amin, E. F. Tan and Z. A. Manan ; *Appl. Catal. B* : Environmental, 43, 57 (2003)
 - 7) J. Shibata, K. Shimizu, A. Satsuma and T. Hattori ; *Appl. Catal. B* : Environmental, 37, 197 (2002)
 - 8) H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata ; *Appl. Catal.*, 70, L 15 (1991)
 - 9) H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata ; *Appl. Catal.*, 75, L 1 (1991)
 - 10) H. Hamada ; *Catal. Today*, 22, 21 (1994)
 - 11) C. Yokoyama and M. Misono ; *Journal of Catalysis*, 150, 9 (1994)
 - 12) Y. Nishizaka and M. Misono ; *Chem. Lett*, 2237 (1994)
 - 13) Y. Guo, M. Sakurai, H. Kameyama, A. Matsuyama and Y. Kudoh ; *Journal of Chemical Engineering of Japan*, 36, 1470 (2003)
 - 14) H. Kameyama ; *Suiso Enerugi Shisutemu*, 20, 16 (1995)
 - 15) K. Murata and H. Kameyama ; *Hyomen Gijutsu*, 47, 173 (1996)
 - 16) H. Kameyama ; *Hyomen Gijutsu*, 48, 994 (1997)
 - 17) A. Iglesias-Juez, A. Martínez-Arias and M. Fernández-García ; *Journal of Catalysis*, 221, 148 (2004)
 - 18) G. Z. Lu, X. Y. Wang, S. L. Wu and R. Ren ; *Journal of East China University of Science and Technology*, 21, 363 (1995)
 - 19) K. Shimizu, H. Maeshima, A. Satsuma and T. Hattori ; *Appl. Catal. B* : Environmental, 18, 163 (1998)
 - 20) F. C. Meunier and J. R. H. Ross ; *Appl. Catal. B* : Environmental, 24, 23 (2000)
 - 21) Y. Kudoh ; US Pat. 6, 302, 935 (2001)
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