

Selective photocatalytic transfer-hydrogenation to 1,5-cyclooctadiene with light transition metal modified rhodium colloid catalyst

Taka-aki Hanaoka^{a,*}, Takehiko Matsuzaki^a, Yoshihiro Sugi^b

^a National Institute of Materials and Chemical Research, AIST Research Center, Tsukuba, Ibaraki 305-8565, Japan

^b Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

Received 8 October 1998; accepted 8 February 1999

Abstract

Effects of additive were examined for the photocatalytic transfer hydrogenation from 2-propanol to 1,5-cyclooctadiene (1,5-COD) with using acetone and $\text{Rh}_4(\text{CO})_{12}$ as a catalyst precursor. Photo-irradiation easily transformed $\text{Rh}_4(\text{CO})_{12}$ to colloidal dispersion in the presence of acetone. Primary particle size of colloid was ca. 2 nm and it formed secondary particles through aggregation. With colloidal rhodium catalyst, the selectivity of cyclooctene (COE) was 86% and the ratio of hydrogenation rate R (= cyclooctadiene to cyclooctene/cyclooctene to cyclooctane) was 4.8. Addition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ enhanced the performance of selective transfer hydrogenation. When Fe salt was used, selectivity reached to 96% and R value decreased to 1.1. The addition of Fe salt did not change primary particle size, but the formation of secondary particle was diminished. Other salt of light transition metal, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, also changed the rate of transfer hydrogenation and R value. These changes were attributable to the change of affinity between surface and substrates causing modification with metal cation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Colloid catalyst; Transfer hydrogenation; Surface modification

1. Introduction

Colloidal metals are attractive catalyst materials as model for both homogeneous and heterogeneous catalysts [1–5]. Especially since the feature of colloid catalyst is considered a heterogeneous catalyst without support, it is ex-

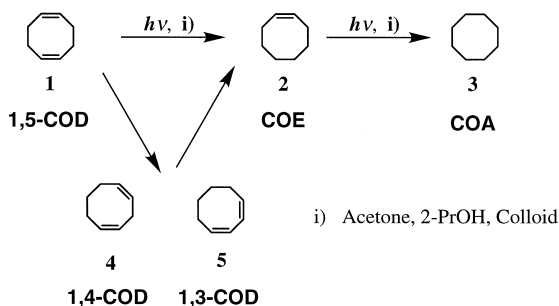
pected to behave a good model of highly dispersed metal catalyst and to show an interesting performance similar to heterogeneous catalyst. Bimetallic colloid has been focused as a new type of colloid catalyst in this decade [6–11]. Although most of studies have dealt with the bimetallic colloid composed of ‘noble metal–noble metal’, for example, Pt–Au [6,7], Pt–Pd [8], Pd–Au [9,10] and Rh–Pd [11], only a limited number of report has dealt with ‘noble metal–light transition metal’ colloid as catalyst [12–15]. Probably it is owing to the difficulty

* Corresponding author. Tel.: +81-298-54-4795; Fax: +81-298-54-4795; E-mail: hanaoka@nimc.go.jp

on the preparation of colloid composed of noble metal and light transition metal. However, in the field of heterogeneous catalysts, considerable effects of light transition metal are well-known as important factors for improvement of catalysis performance [16].

Noble metal colloid is known as a catalyst for photo hydrogen formation from aqueous solution with using aryl ketone [17–20]. Almost all these studies have mainly aimed solar energy conversion in aqueous solution, not aimed applying to organic synthesis in non-aqueous solution. We have been investigated the preparation of colloidal noble metal without addition of stabilizer, and their applications as photo related catalysts. The systems consisting of colloidal noble metals and triplet sensitizer were effective as photocatalysts on dehydrogenative dimerization of alcohols and cyclic ethers [21–23]. These systems were also applicable for a photocatalytic transfer hydrogenation of 1,5-cyclooctadiene (1,5-COD, **1**) to cyclooctene (COE, **2**) and cyclooctane (COA, **3**) in the presence of acetone and 2-propanol [24] (Scheme 1).

On the basis of the knowledge of heterogeneous catalysts, we attempted the modification of rhodium colloid catalysts with the light transition metals. In this paper, we will report selective hydrogenation of 1,5-COD by the modified rhodium colloid catalysts, and the effects of addition of light transition metal.



Scheme 1. Reaction path of photocatalytic transfer hydrogenation of 1,5-COD.

2. Experimental

All materials purchased were used without further purification. TEM (transmission electron microscope) photographs of colloidal particles were obtained with Hitachi H-800 transmission electron micrograph. UV–VIS spectra were measured with Shimadzu MPS-2000 type spectrometer.

Typical photocatalytic transfer hydrogenation of 1,5-COD with 2-propanol was carried out as described below. Three milligrams of $\text{Rh}_4(\text{CO})_{12}$ (0.016 mmol as Rh), acetone (8 cm³), 2-propanol (32 cm³) and internal standard (*n*-pentadecane) were placed in a 40-cm³ cylindrical quartz cell. The solution was deaerated by nitrogen bubbling before irradiation. Reaction cell was irradiated with a 500-W high pressure mercury lamp (*Ushio*) through UV-25 short-cut filter (*Toshiba*, 40% transmission at 250 nm) in a water bath (20°C). Evolved gas was corrected by a buret. After an appropriate time, 1,5-COD (0.2 cm³) was added to the reaction solution and the liquid phase products were analyzed with gas chromatograph at an interval time. The structures of all products were confirmed by comparison with authentic samples.

In the experiments using additive, all metal salts were put into the reaction solution before irradiation and they were confirmed to be dissolved completely. Photocatalytic transfer hydrogenations were carried out with same manner of rhodium colloid catalysts.

3. Results

After a short period of irradiation to reaction solution containing $\text{Rh}_4(\text{CO})_{12}$, its color was changed from rose red to dark brown, and hydrogen gas evolution started. The change of color was assigned to form colloidal particle from $\text{Rh}_4(\text{CO})_{12}$ by irradiation. Fig. 1 showed the change of UV–VIS spectra. Characteristic absorption of $\text{Rh}_4(\text{CO})_{12}$ around 350 nm disappeared and a broad absorption band extended to

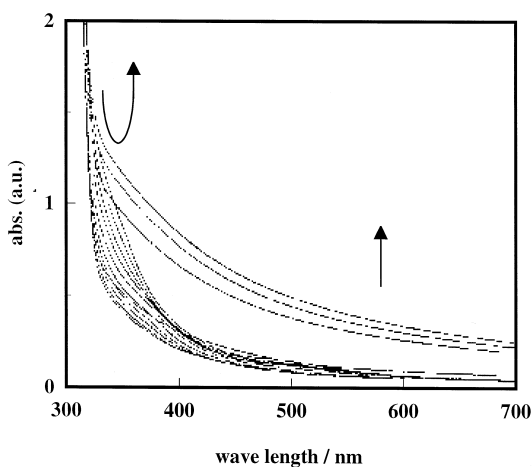


Fig. 1. Change of UV-VIS spectrum of 2-propanol-acetone- $\text{Rh}_4(\text{CO})_{12}$ solution through irradiation. Reaction condition: 2-propanol: 32 ml, acetone: 8 ml, $\text{Rh}_4(\text{CO})_{12}$: 3.0 mg, at 20°C, under N_2 . Spectra was taken at 0, 0.5, 1, 2, 4, 6, 8, 10, 13, 16, 20, 24, 28, 32 min irradiated.

long wavelength appeared. New absorption is attributed to a scattering band caused by highly dispersed colloidal metal. Although a stabilizer, such as surfactant or polymer, were not used, the colloid solution was stable during the reaction.

After an enough period for complete conversion of $\text{Rh}_4(\text{CO})_{12}$ to colloid, 1,5-COD was

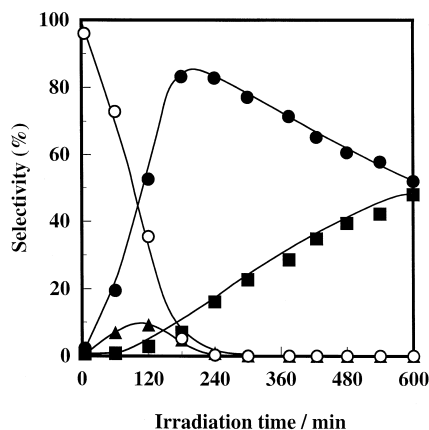


Fig. 2. Time course of products selectivity on photocatalytic transfer hydrogenation of 1,5-COD with Rh colloid catalyst. (■) COA, (●) COE, (▲) 1,4-COD, (○) 1,5-COD. Reaction condition: 2-propanol: 32 ml, acetone: 8 ml, $\text{Rh}_4(\text{CO})_{12}$: 3.0 mg, at 20°C, under N_2 .

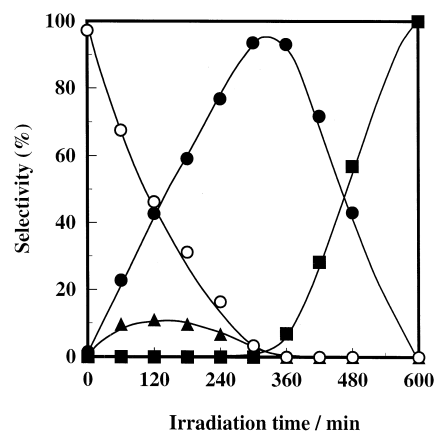


Fig. 3. Time course of products selectivity on photocatalytic transfer hydrogenation of 1,5-COD with Rh-Fe (4:1) colloid catalyst. (■) COA, (●) COE, (▲) 1,4-COD, (○) 1,5-COD. Reaction condition: 2-propanol: 32 ml, acetone: 8 ml, $\text{Rh}_4(\text{CO})_{12}$: 3.0 mg, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: 1.5 mg, at 20°C, under N_2 .

added to a reaction solution. Fig. 2 showed the time course on photocatalytic transfer hydrogenation of 1,5-COD with $\text{Rh}_4(\text{CO})_{12}$ as a precursor of catalyst. Addition of 1,5-COD decreased H_2 evolution rate by approximately 70% of before addition. 1,5-COD was isomerized to 1,4-cyclooctadiene (1,4-COD, **4**) and 1,3-cyclooctadiene (1,3-COD, **5**), and cyclooctadienes were simultaneously hydrogenated to COE. Prolonged irradiation gave COA by successive transfer hydrogenation. The amount of 1,3-COD was neglected due to high reactivity for hydrogenation. Maximum selectivity of COE reached to 86%. The ratio of two step hydrogenation rates (R), 'COD to COE'/'COE to COA', was ca. 4.8, namely hydrogenation of COE was much harder than that of COD.¹ Therefore, high selectivity of COE is attributable to the difference of hydrogenation rate among substrates. The yields of hydrogenated products slightly decreased by following photochemical reactions.

Addition of a light transition metal salt changed a feature of transfer hydrogenation.

¹ These ratio were calculated from the slopes of the decrease of compounds.

Table 1

Effect of additive amount on photocatalytic transfer hydrogenation of 1,5-COD with $\text{Rh}_4(\text{CO})_{12}\text{-FeCl}_3 \cdot 9\text{H}_2\text{O}$ catalyst

$\text{Rh}_4(\text{CO})_{12}$ (mg)	$\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$ (mg)	Fe/Rh (mol/mol)	H_2 evolution rate (1st stage) (mmol/min)	R [(COD to COE)/ (COE to COA)]	Max selectivity of COE (%)
3.0	0.0	–	0.051	5.5	86
	0.5	0.08	0.012	15.0	94
	1.5	0.23	0.014	1.1	94
	3.0	0.48	0.006	1.1	94

Reaction condition: 2-propanol: 32 ml, acetone: 8 ml, at 20°C, under N_2 . H_2 evolution rate was evaluated before addition of olefine. R were determined from the slope of the decrease of compounds.

Particularly, the modification with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ enhanced the selectivity of COE. The time course of the reaction with rhodium colloid promoted with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fe/Rh = ca. 0.25) was illustrated in Fig. 3. This reaction has three points of peculiarity compared to the experiment without Fe salt. (1) Addition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ increased the rate of hydrogenation for both steps, 'COD to COE' and 'COE to COA', especially the latter step was highly accelerated. As the result, the value of the rate ratio R , drastically decreased to be close on unity. (2) The maximum selectivity of COE reached up to 94%, since hydrogenation of COE did not proceed during COD remained in the reaction solution. It means COD prevented transfer hydrogenation of COE. (3) Hydrogen gas evolution was depressed by the addition of Fe salt.

As shown in Table 1, variation of additive amount gave different behavior on transfer hydrogenation of 1,5-COD. Small amount of Fe salt (Fe/Rh = ca. 0.08) effectively retarded the hydrogen evolution and decreased the rate of transfer hydrogenation for 'COE to COA'.

However, R value increased up to 15, since the rate for 'COD to COE' was kept in the same level before addition of Fe salt. On the other hand, the addition of Fe salt over 25 mol% to rhodium atom highly accelerated hydrogenation of 'COE to COA', and R value decreased to 1.1. In both cases, the maximum selectivities of COE were 94%, but the reasons for increase of selectivities were different.

Other light transition metal salts also affected on transfer hydrogenation of 1,5-COD. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ showed an effect similar to $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ considerably reduced the activity of transfer hydrogenation of COE. The maximum selectivities of COE were 91% and 89%, and the R values varied to ca. 1 and 10, with addition of Ni and Cu salt, respectively (Table 2).

Fig. 4 showed TEM photograph of reaction solution with $\text{Rh}_4(\text{CO})_{12}$. Colloidal particles that have a diameter of ca. 2 nm were found as primary particles. These particles gathered each other to form secondary particles that have a diameter of ca. 20 nm. Secondary particles formed chain and aggregation and the primary

Table 2

Additive effect by light transition metal salt on the photocatalytic transfer hydrogenation of 1,5-COD with $\text{Rh}_4(\text{CO})_{12}$ as a precursor of catalyst

$\text{Rh}_4(\text{CO})_{12}$ (mg)	Additive	Rh/additive (mol/mol)	H_2 evolution rate (1st stage) (mmol/min)	R [(COD to COE)/ (COE to COA)]	Max selectivity of COE (%)
3.0	none	–	0.051	5.5	86
	$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	4.2	0.031	9.0	89
	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.1	0.030	1.3	91

Reaction condition: 2-propanol: 32 ml, acetone: 8 ml, at 20°C, under N_2 . H_2 evolution rate was evaluated before addition of olefine. R were calculated from the slopes of the decrease of compounds.

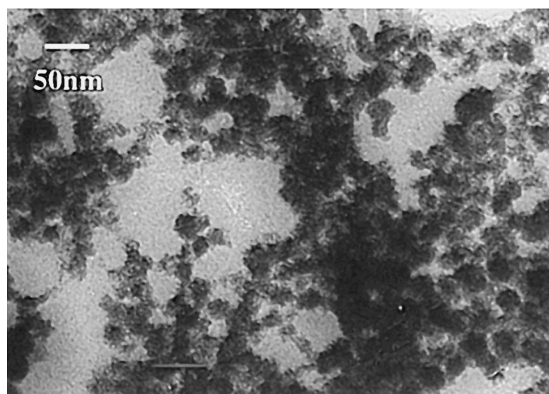


Fig. 4. Transmission electron micrograph of colloidal catalyst species prepared from $\text{Rh}_4(\text{CO})_{12}$ in acetone and 2-propanol through photoreaction.

particles were dispersed among them. A solution containing rhodium and iron gave another type of dispersion as shown in Fig. 5. The colloidal particles that have nearly same diameters with above were separated well each other and aggregated secondary particles were not observed. The difference caused by the modification of the surface nature of particles.

4. Discussion

Scheme 2 exhibited a proposed cycle of the photocatalytic transfer hydrogenation of 1,5-COD [24]. This system consists of an alcohol as a hydrogen donor, acetone as a triplet sensitizer and a colloid catalyst. Colloid catalyst is formed photochemically from a metal complex in the reaction solution. Irradiation is also necessary to carry out the transfer hydrogenation from alcohol to substrates. The photocatalytic transfer hydrogenation requires photo excitation of acetone to abstract hydrogen atom from alcohol. The abstracted hydrogen atom further transfers to rhodium colloid. Hydrogen species successively generate hydrogen gas or transfer to olefin adsorbed on the surface of colloid. Since the transfer hydrogenation of olefin occurs on the surface between absorbed species, the surface

nature of colloid determines the catalytic performances. Therefore, the change of reaction feature in this study by the additive is attributable to the modification of colloid surface.

As shown in Fig. 1, the UV–VIS spectra indicated that $\text{Rh}_4(\text{CO})_{12}$ easily decomposed and colloidal dispersion was formed during a short period of irradiation. However, light transition metal cation such as Fe^{3+} is difficult to be reduced to metallic state. Since noble metal colloid works as an electron pool [25], these particles charge negatively under irradiation. Consequently, it is rational that the cation of light transition metal, such as Fe^{3+} , adsorbed on the surface of rhodium colloid. This type of modification of surface causes electrostatic repulsion among particles and prevents aggregation of colloids as shown in Fig. 5. Otherwise, if Fe cation is reduced to metallic state under the irradiation, it is possible to form Rh–Fe alloy or doubly shelled colloid [26] as like as Pd–Cu and Pt–Ni [12–15]. To decide the state of additive cation, further study is required.

Influence of Fe addition on the transfer hydrogenation was summarized to two features. One is a promotion of hydrogenation ability for olefins. The additive accelerated transfer hydrogenation of both ‘COD to COE’ and ‘COE to COA’, and decreased R value close to unity.

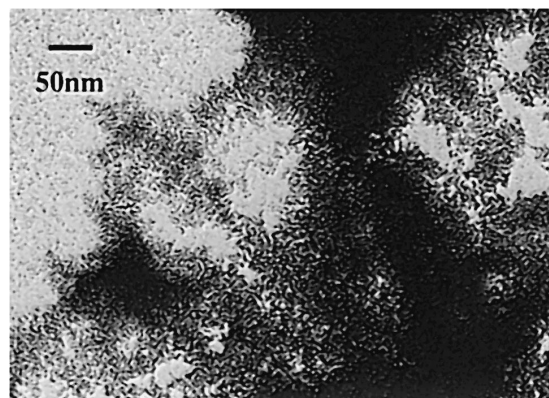
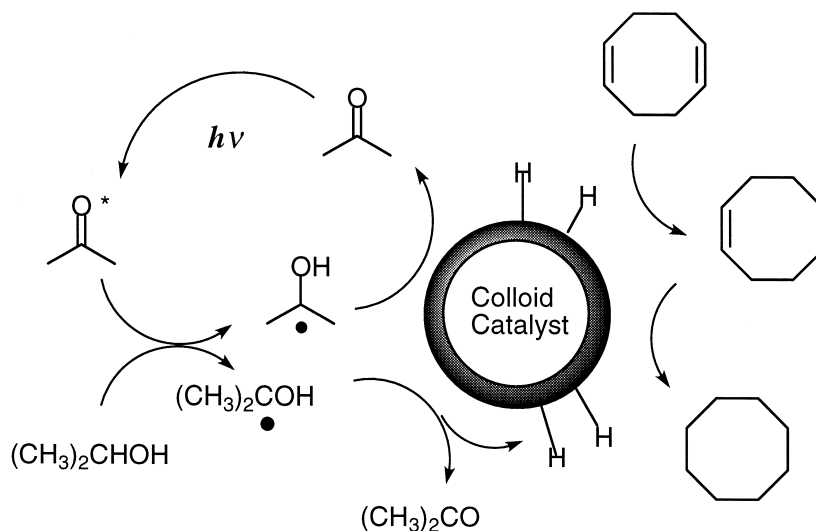


Fig. 5. Transmission electron micrograph of colloidal catalyst species prepared from $\text{Rh}_4(\text{CO})_{12}-\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Rh/Fe = 4/1) in acetone and 2-propanol through photoreaction.



Scheme 2. Proposed reaction mechanism for photocatalytic transfer hydrogenation of 1,5-COD.

This effect is attributable to similar effect of Fe on the hydrogenation of carbon monoxide with rhodium catalyst supported on silica [27–31]. Second point is change of affinity between the surface and olefins. It is known that diolefin is easily hydrogenated compared to mono-olefin owing to the difference of affinity against the surface of catalyst. Prevention of transfer hydrogenation of COE under existence of 1,5-COD means that an affinity of 1,5-COD toward the surface is much stronger compared to that of COE. Consequently, access of COE to the catalyst surface is blocked by the strongly adsorbed 1,5-COD through a competitive adsorption. In the case of colloidal rhodium catalyst, transfer hydrogenation of COE began when 50% of 1,5-COD were consumed. It indicates that the difference of affinities against the surface between 1,5-COD and COE was originally small on colloidal rhodium catalyst, however it was enlarged by modification with Fe. Therefore, the high selectivity of COE was realized by the recognition of substrates on the modified surface of catalyst with Fe, not by the difference of hydrogenation rate between the substrates. The effects on the transfer hydrogenation by the addition of other light transition metal salts, Cu

and Ni, were also plausible to be modification of the colloid surface.

5. Conclusion

We found that modification of rhodium colloid with light transition metal effectively changed the feature of photocatalytic transfer hydrogenation of 1,5-COD, and the selectivity of COE varied by the addition of them. Especially, Fe salt accelerated the rate of transfer hydrogenation for ‘COE to COA’, and the selectivity of COE reached up to 94%. Addition of metal salt changed the affinity between the surface and the substrates through adsorption of cation on the surface. However, the oxidized state of additive metals and the structure of modified colloids are unclear in our study, yet. We are trying to determine the state, for example by Mössbauer experiments.

Colloidal catalyst has a benefit to evaluate a nature of metallic catalyst because of lack of an interaction with support. We supposed an effect of additive on the performances of colloid catalyst was one of the clue to understand of addi-

tive effects on heterogeneous metal supported catalysts.

References

- [1] H. Hirai, N. Toshima, in: Y. Iwasawa (Ed.), Tailored Metal Catalysts, Reidel, Tokyo, 1986, p. 87.
- [2] J.S. Baradley, E. Hill, M.E. Leonowicz, H. Witzke, J. Mol. Catal. 41 (1987) 59.
- [3] A. Henglein, Chem. Rev. 89 (1989) 1861.
- [4] G. Schmid, Chem. Rev. 92 (1992) 1709.
- [5] H. Bönemann, W. Brijoux, R. Brinkmann, E. Dinjus, R. Fretzen, T. Joussen, B. Korall, J. Mol. Catal. 74 (1992) 323.
- [6] P.A. Sermon, J.M. Thomas, K. Keryou, G.R. Millward, Angew. Chem. Int. Ed. Engl. 26 (1987) 918.
- [7] A. Harriman, J. Chem. Soc., Chem. Commun. (1990) 24.
- [8] N. Toshima, T. Yonezawa, M. Harada, K. Asakura, Y. Iwasawa, Chem. Lett. (1990) 815.
- [9] H. Liu, G. Mao, S. Meng, J. Mol. Catal. 74 (1992) 275.
- [10] N. Toshima, M. Harada, Y. Yamazaki, K. Asakura, J. Phys. Chem. 96 (1992) 9927.
- [11] M. Harada, K. Asakura, Y. Ueki, N. Toshima, J. Phys. Chem. 97 (1993) 10742.
- [12] J.L. Marignier, J. Belloni, M.O. Delcourt, J.P. Chevalier, Nature 317 (1985) 344.
- [13] N. Toshima, Y. Wang, Chem. Lett. (1993) 1611.
- [14] N. Toshima, T. Yonezawa, K. Nakata, P. Lu, K. Hirakawa, H. Kitoh, Photon factory activity report, KEK Tsukuba 13 (1996) 126.
- [15] N. Toshima, Y. Wang, Langmuir 10 (1994) 4574.
- [16] J.H. Shinfelt, Acc. Chem. Res. 10 (1977) 15.
- [17] C.K. Grätzel, M. Grätzel, J. Am. Chem. Soc. 101 (1979) 7741.
- [18] A. Harriman, J. Chem. Soc., Faraday Trans. II 82 (1986) 2267.
- [19] C.-K. Tan, V. Newberry, T.R. Webb, C.A. McAuliffe, J. Chem. Soc., Dalton Trans. (1987) 1299.
- [20] I. Willner, R. Maidan, D. Mandler, H. Dürr, G. Dörr, K. Zengerle, J. Am. Chem. Soc. 109 (1987) 6080.
- [21] H. Arakawa, Y. Sugi, Chem. Lett. (1981) 1323.
- [22] H. Arakawa, Y. Sugi, K. Takeuchi, K. Bando, Y. Takami, Shokubai (Catalyst) 25 (1985) 392.
- [23] T. Hanaoka, H. Arakawa, K. Takeuchi, T. Matsuzaki, Y. Sugi, Chem. Express 4 (1989) 137.
- [24] T. Hanaoka, Y. Kubota, T. Takeuchi, T. Matsuzaki, Y. Sugi, J. Mol. Catal. A 98 (1995) 157.
- [25] A. Henglein, B. Lindig, J. Westerhausen, J. Phys. Chem. 85 (1981) 1627.
- [26] Z. Duan, M.J. Hampden-Smith, A. Datye, P. nigrey, C. Quintana, A.P. Sylwerster, J. Catal. 139 (1993) 504.
- [27] H. Arakawa, T. Hanaoka, K. Takeuchi, T. Matsuzaki, Y. Sugi, in: M.J. Phillips, M. Ternan (Eds.), Proc. 9th Congress Catal., Vol. II, The Chemical Institute of Canada, Cargary, 1988, p. 602.
- [28] R. Burch, M.I. Petch, Appl. Catal. A 88 (1992) 61.
- [29] L.E.Y. Nonneman, A.G.T.M. Bastein, V. Ponec, Appl. Catal. 62 (1990) L23.
- [30] E. Guglielminotti, F. Pinna, M. Rigoni, G. Strukul, L. Zanderighi, J. Mol. Catal. A 103 (1995) 105.
- [31] H. Arakawa, T. Fukushima, M. Ichikawa, S. Natsushita, K. Takeuchi, T. Matsuzaki, Y. Sugi, Chem. Lett. (1985) 881.