

**RELATIONSHIP BETWEEN OZONE FORMATION AND
TOLUENE DECOMPOSITION EFFICIENCY
IN A ZEOLITE-HYBRID PLASMA REACTOR**

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ABSTRACT

A zeolite-hybrid plasma reactor showed the excellent performance for the toluene decomposition by the cyclic operations such as long time toluene adsorption followed by short time plasma discharge. In particular, the decomposition efficiency of toluene was enhanced by placing the zeolite in the downward position of the plasma region rather than placing that in the upward position. On the other hand, it was found that the fast electron could not reach in the internal area of the zeolite, which was effective for VOCs plasma decomposition in gas phase. Then, we investigated the reaction mechanism related to active oxygen species by tracing the behavior of ozone formed in the reactor. Actually, the formation of ozone was suppressed in the zeolite-filled region, although the concentration of ozone formed in the plasma region gradually increased in the gas flow direction. That is, the toluene adsorbed on the zeolite was scarcely decomposed in the upward position, while it was readily decomposed in the downward position. These results can be well explained the positioning effect of zeolites, and lead to the conclusion that the synergistic effect of plasma and zeolite was substantially ascribed to the following mechanism; active oxygen species formed by the plasma diffused easily into the micropore, and then promoted the decomposition of $C_6H_5CH_3$ adsorbed in the internal area.

INTRODUCTION

Nonthermal plasma processes have attracted significant interest as a promising technology for removing volatile organic compounds (VOCs) [1]. Over the last decade, many researchers have been trying to improve the process efficiency to decompose VOCs using various plasma reactors, such as pulsed corona [2-4], ferroelectric pellet packed-bed discharge [5], silent (dielectric barrier) discharge [6], and surface discharge [7, 8] reactors. The feasibility of plasma processes is limited by energy efficiency and the formation of toxic byproducts. To improve the energy efficiency and CO₂ selectivity, a catalyst-combined plasma reactor was recently designed [9-11]. We have also proposed a nonthermal plasma reactor combined with an adsorbent [8, 12] and its cyclic plasma operation [13]; VOCs could be removed by adsorption on the zeolite without energy consumption in plasma-off time, and this was followed by rapid oxidation during a short plasma-on time.

In this work, we focused on the reaction mechanism. In particular, in order to clarify the synergistic effect between plasma and zeolite, the enhancement effect for the toluene decomposition by a zeolite-hybrid reactor was discussed based on the property of zeolites, and the role and behavior of ozone as significant active species was investigated in detail.

EXPERIMENTAL

Experimental setup

Decomposition of toluene (C₇H₈)

The configuration of a surface discharge reactor is illustrated in Fig. 1. A quartz tube (i.d.: 10 mm, thickness: 1.5 mm) was used as a dielectric barrier. A spiral platinum wire coil (70 turns in 150 mm) with a 0.3-mm diameter was set in contact with the inner wall of the barrier tube. A copper foil was wrapped on the outside of the barrier tube as the ground electrode, and the outer electrode length was 100 mm.

When zeolites were combined with the plasma reactor, i.e., a zeolite-hybrid reactor, zeolite pellets were placed in the positions of (a) or (b) in the figure. On the basis of the positions in the gas flow direction, these hybrid reactors were called "upward type" and "downward type" in this work.

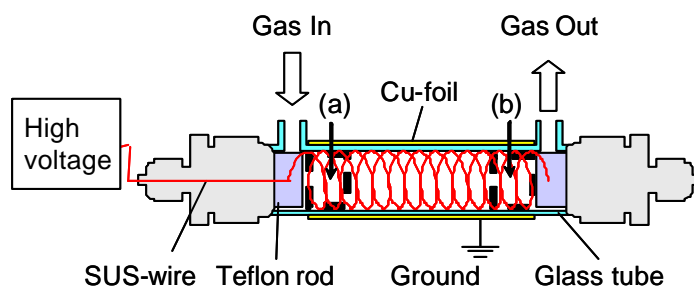


Figure 1: Configuration of a zeolite hybrid reactor.

The reactant gas consisting of 200 ppm C₇H₈, 0.5% H₂O, and 20.0% O₂, with N₂ making up the remaining fraction, was fed into the reactor at a flow rate of 500 cm³/min, where a high AC voltage was applied between the two electrodes. Plasma energy was supplied using an AC high-voltage neon transformer (24kHz, NEON M-5, LECIP Co., Japan) and the plug-in power was measured using a digital power meter (WT110, Yokogawa Electric Co., Japan).

The plasma was turned on and off periodically four times for a total of 160 min (off for 30 min ? on for 10 min ? off for 30 min ? etc.), because cyclic operation improves the energy efficiency, i.e., adsorption followed by plasma decomposition [8, 13].

The effluent gas was measured continuously using a Fourier-transform infrared spectrometer (FT-IR, FTS135, Bio-Rad Laboratories, USA) equipped with a gas cell (2.4-m-long path, 125 cm³ volume, Infrared Analysis Inc., USA) and the total amounts of products were calculated from the integrated spectra for each component. The amounts of adsorbed components on the zeolite were measured using temperature-programmed desorption and oxidation (TPD and TPO). For the TPD process, the zeolite was heated to 500 °C at a rate of 10 °C/min and held at that temperature under a N₂ atmosphere. After the TPD process, the residual solid carbon was oxidized at 600 °C under the dry air (20% O₂ and 80% N₂). The decomposition efficiency was evaluated using the following equations:

$$\text{C}_7\text{H}_8 \text{ decomposition } [\%] = \{(\text{C}_7\text{H}_8)_{\text{in}} - (\text{C}_7\text{H}_8)_{\text{out}} - (\text{C}_7\text{H}_8)_{\text{TPD}}\} / \{(\text{C}_7\text{H}_8)_{\text{in}}\} \times 100$$

where (C₇H₈)_{in} and (C₇H₈)_{out} are the total input and output of toluene, respectively. (C₇H₈)_{TPD} is the amount of toluene desorbed from the TPD reactor, where the adsorbed toluene could be easily desorbed from the zeolite surface without noticeable decomposition.

Measurement of ozone (O₃) concentration in a reactor

The reactor having 6 branch pipes as shown in Fig.2 was used for the measurement of O₃ distribution in the plasma region. The gas was sampling from each branch pipe by a diaphragm pump, followed by measuring O₃ using an ozone-monitor (PG-620H, Ebara Jitsugyo Co., Ltd., Japan). The zeolite pellets of 1.0g were filled the position indicated in the dotted line. When the gas flow direction was chosen "Forward" and "Reverse", the zeolite position become the arrangement of "upward type" and "downward type", respectively. In this experiment, the dry air was introduced into the reactor at a flow rate of 500 cm³/min, and the input power of 2.0W was applied.

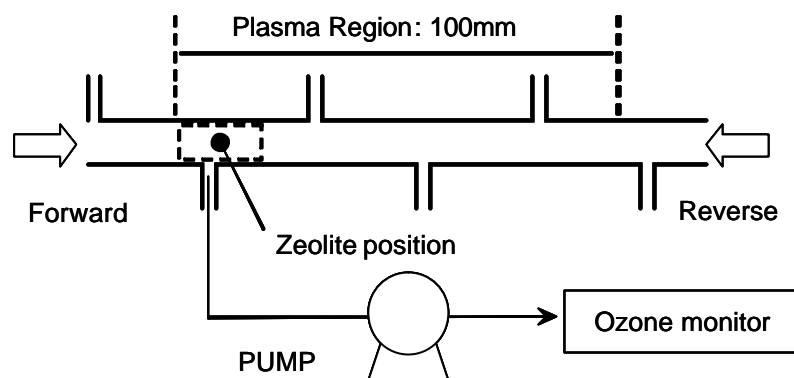


Figure 2: Configuration of reactor for the monitoring of the ozone distribution in the plasma region.

Zeolite pellets

Four types of zeolites were used in this work; Na-forms of faujasite (Na-Y) , two types of H-forms of faujasite (H-Y), H-forms of mordenite (MOR), and H-forms of ferrierite (FER). These samples molded in the pellet were purchased from Tosoh Co. and Nikky-Universal Co. Ltd.

RESULTS AND DISCUSSION

Enhancement effect for toluene decomposition and basic properties of zeolites

We reported that the energy efficiency on VOCs plasma decomposition was enhanced by combining with zeolite-pellets, i.e., using a zeolite-hybrid plasma reactor [8, 12, 13]. The enhancement effect was greatly different by zeolite types and its position in the reactor [12, 13]. Table 1 summarizes the decomposition efficiency, zeolite types and its basic properties. The decomposition efficiency in the downward type was larger 3.7 times than that in a conventional type reactor, while that in the upward type was 1.2-1.5 times. If their effects occur simply from plasma and the solid surface activated by plasma, the decomposition efficiency does not depend on the position of zeolites. However, the positioning effect was observed on Na-Y, H-Y and MOR. In particular, the decomposition efficiency in the downward type differed greatly from zeolite to zeolite. The synergistic effect between plasma and zeolite was considered based on the following zeolite-properties: the crystal structure (size of the micropore), specific surface area (BET), and acidic property of the solid surface.

Table 1: Decomposition efficiency in the hybrid plasma reactors and property of zeolites.

Zeolite	C ₇ H ₈ decomp. [%]		Surface area(m ² /g)	SiO ₂ /Al ₂ O ₃	Channel. . .
none	15		.	.	.
Na-Y	21, Up,	52, Down,	750	3.1	7.4
H-Y(1)	18	55	650	1.9	7.4
H-Y(2)	20	50	520	5.6	7.4
MOR	23	35	460	15.2	6.7 , 7.0
FER	19	20	270	17.9	4.3 , 5.5

Crystal structure of zeolites

It is worth noting that the enhancement effect in the FER-hybrid reactor was independent of the zeolite positions. FER is different from other zeolites in the size of the micropore (Channel). The function of molecular sieving is one of the significant properties of zeolites, owing to the well-defined crystal structure and the micropore. According to this function, C₆H₅CH₃ (ca. 6 angstrom) do not reach in the internal area of FER through the micropore (4.3 x 5.5 angstrom). In contrast, the considerable amounts of C₆H₅CH₃ may be adsorbed in the internal area of Na-Y, H-Y and MOR (See table 1). In the upward type reactor, the enhancement effect was not so different between FER and the others, and not so large. These results suggested that most of C₆H₅CH₃ adsorbed in the internal area did not decompose. In other word, the fast electron could not reach in the internal area, which was effective for VOC decomposition on the gas phase plasma reaction.

Specific surface area of zeolites

At the beginning of this research, we expected the role of zeolites as an adsorbent. The specific surface area (surface area) of the zeolite is different by compositions, crystal types, synthetic methods, binders and so forth. In general, the larger the surface area is, the larger the adsorption capacity is.

In the downward type (table 1), the higher the decomposition efficiency was, the larger the surface area was. However, the data of the surface area is based on a value measured by the BET adsorption method of N₂ (3.2 angstrom). For example, it is not possible to identically compare the value of FER in which C₆H₅CH₃ can not adsorb in the internal area as mentioned before. Then, the relationship between the amount of C₆H₅CH₃ adsorbed on the zeolite and the decomposition efficiency was investigated. As shown in Fig. 3, the strong correlation was observed in the downward type, while no any correlation in the upward type; these are relative values to compare with the result under a conventional plasma reactor.

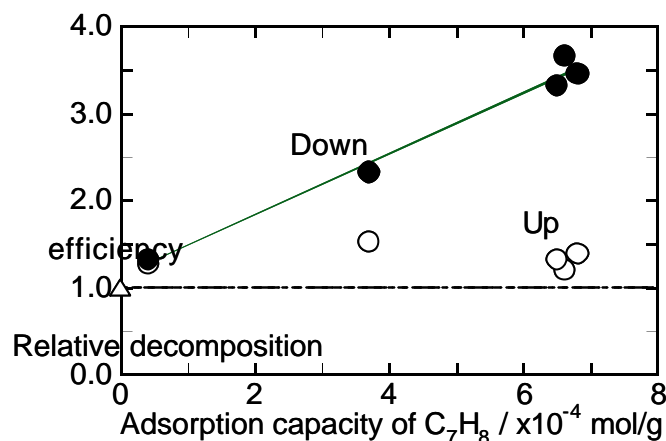


Figure 3 Relationship between decomposition efficiency and adsorption capacity.

Acidic property

Besides the character as an adsorbent, the acidic property of the zeolite surface is revealed in many catalytic reactions. The acid amount and acid strength depend on a kind of cation/proton and a ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the zeolite framework. As shown in table 1, however, the character as a catalyst did not affect the decomposition efficiency under plasma discharge. These findings lead us to believe that the zeolite acts mainly as an adsorbent in the hybrid plasma reactor.

Role of ozone as active species

Since the fast electron can not reach in the internal area, any activated species form by plasma may play an important role in the plasma reactor. Therefore, we investigated the behavior of O_3 in the zeolite-hybrid reactor, because O_3 was detectable species among active chemical species expected under a plasma atmosphere. In the preliminary experiments, it was also known that $\text{C}_6\text{H}_5\text{CH}_3$ concentrated on H-Y decomposed easily by introducing O_3 [12, 13].

Figure 4 shows the relationship between the decomposition efficiency and the O_3 concentration after the reaction; these are relative values to compare with the result under the conventional plasma reactor. The decomposition efficiency in the downward type increased noticeably with the decrease of O_3 , while that in the upward type did not depend on O_3 concentration. It was suggested that O_3 formed by plasma diffused easily into the micropore, and then promoted the decomposition of $\text{C}_6\text{H}_5\text{CH}_3$ adsorbed in the internal area.

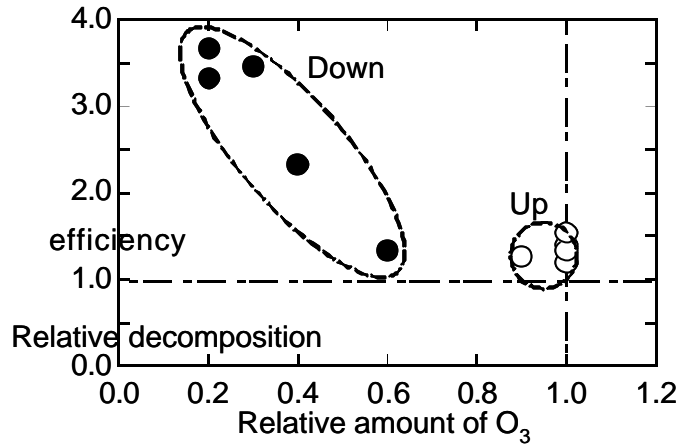


Figure 4: Relationship between relative decomposition efficiency and relative amount of ozone.

Role of zeolites and distribution of ozone in a plasma reactor

The behavior of O_3 formation was investigated using the reactor as shown in Fig. 2. The distribution of O_3 in the reactor in the absence of $C_6H_5CH_3$ and H_2O is shown in Fig. 5 (a) and (b). When the gas flow direction was chosen "Forward" and "Reverse", the reactor arrangement became "upward type" and "downward type", respectively. Ozone formed immediately in the edge (0 or 100 mm) of the ground electrode, and its concentration gradually increased in the flow direction of gas. In the conventional type, i.e., without zeolites, the same results were definitely obtained independent of the flow direction. The average of O_3 concentration was shown in the dotted line.

Figure 6 shows the distribution of O_3 concentration in the hybrid reactor with H-Y of 1.0g during plasma discharge. The dotted line shows the result without the zeolite, again. When H-

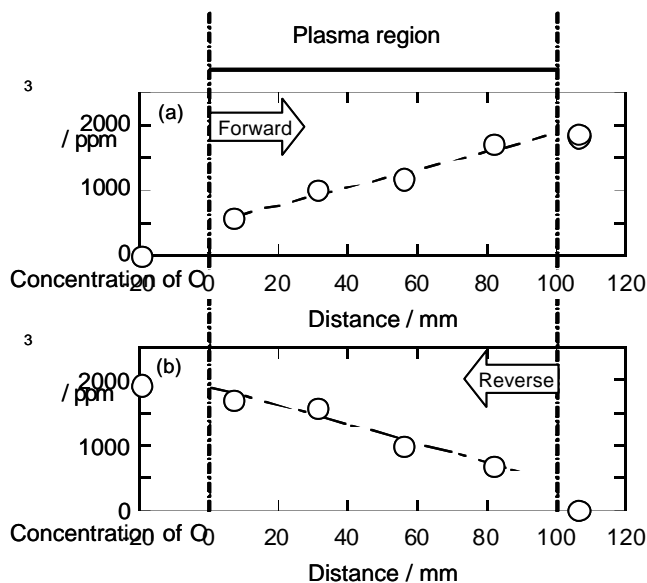


Figure 5: Ozone distribution in the conventional plasma reactor: (a) Forward and (b) Reverse.

Y was placed in the upward position, O_3 was not observed in the filled region at all. The

change of O_3 concentration was not observed when the zeolite was placed in the downward position. The same results were observed even in the case of FER. These findings show that the formation of O_3 was suppressed strongly in the region filled with zeolites.

Regardless of the upward and downward positions, the amount of $C_6H_5CH_3$ adsorbed on the zeolite was the same, i.e., the adsorption time for 30 min before plasma discharge. However, the decomposition efficiency in the upward type did not depend on the type of the zeolite (table 1), and was equal to or lower than that in the downward type. The zeolite in the upward position seemed to be not obtained enough O_3 to decompose the $C_6H_5CH_3$ adsorbed. Therefore, reaction mechanism in the upward type was mainly the direct plasma decomposition of $C_6H_5CH_3$ in gas phase. Furthermore, the additional effect might be occurred from the decomposition of $C_6H_5CH_3$ adsorbed on the external sites of zeolites. It was reported that, in Na-Y, the external surface area is less than 5% of the total surface area [14]. In addition, it was also known that not only micropores but also macropores (300-1000 nm) were created in zeolite pellets, since small amounts of binder were used in the molding of zeolites [15, 16]. By the way, a lot of O_3 existed in the downstream position enough to decompose $C_6H_5CH_3$ adsorbed in the internal area.

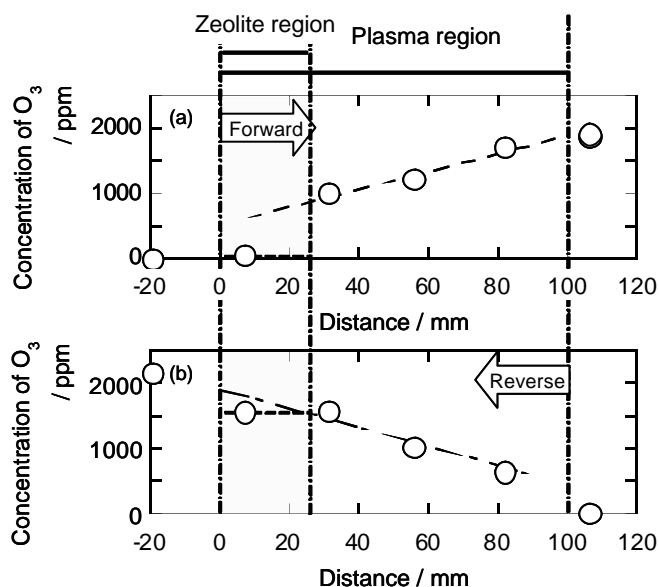


Figure 6: Ozone distribution in the zeolite-hybrid plasma reactor: (a) Forward and (b) Reverse.

Reactivity of toluene adsorbed on zeolites

It is well-known that the oxidation ability of O_3 for VOCs is not so high, e.g., O_3 can not oxidize $C_6H_5CH_3$ directly in gas phase. However, $C_6H_5CH_3$ adsorbed on H-Y was easily decomposed by O_3 in the zeolite-hybrid plasma reactor of downward type [13]. In the case of VOCs oxidation by O_3 on catalysts, it was reported that the atomic oxygen were derived from O_3 decomposition on catalysts, and then followed by oxidizing VOCs [17]. These catalysts are required the appropriate decomposition ability for O_3 .

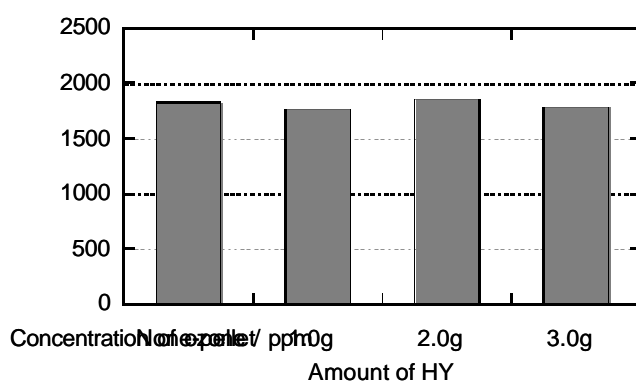


Figure 7: Concentration of ozone at the downstream of the zeolite layers: (a) none, (b) 1.0g, (c) 2.0g and (d) 3.0g.

The decomposition of O_3 was investigated on H-Y. Figure 7 shows the concentration of O_3 in the downstream of the H-Y beds in which 1.0 to 3.0g of H-Y were filled. The decomposition of O_3 was not observed at all. We can not accept the mechanism based on VOCs oxidation by O_3 on the zeolite as a catalyst. That is, it should be pointed out that the chemical bond of the $C_6H_5CH_3$ molecule was weakened by strongly adsorbing on the solid surface. The micropore of zeolites as a catalyst was expected not only the function of molecular sieving but also the reaction space having a specific electric field derived from well-defined crystal structure. These results suggested that $C_6H_5CH_3$ adsorbed strongly on the zeolite easily decomposed even by gas phase O_3 .

CONCLUSIONS

The enhancement effect for toluene decomposition was greatly different by the position and the type of the zeolite in the zeolite-hybrid plasma reactor. From the relationship between the decomposition efficiency and the properties of zeolites, the following results were obtained.

- i) The decomposition efficiency of toluene was enhanced by placing the zeolite in the downward position of the plasma region rather than placing that in the upward position.
- ii) The fast electron could not reach in the internal area of the zeolite, which was effective for VOC plasma decomposition in gas phase.

- iii) A part of the enhancement effect derived from the decomposition of $C_6H_5CH_3$ adsorbed on the external area of zeolite.
- iv) Ozone formed by the plasma diffused easily into the micropore, and then promoted the decomposition of toluene adsorbed in the internal area.
- v) The chemical bond of toluene molecule was weakened by strongly adsorbing to the solid surface. In other word, toluene adsorbed on the zeolite easily decomposed even by gas phase O_3 .
- vi) The major synergetic effect in the zeolite-hybrid plasma reactor occurred from the decomposition of toluene adsorbed in the internal area by active oxygen species.

Besides ozone, it can not exclude the involvement of undetectable active oxygen species such as O^- , O_2^- , O_3^- , OH radical, and so forth under a plasma atmosphere.

REFERENCES

1. Oda T. (2003). J. Electrostat. **57**, 293-311, 2003.
2. Nunez C. M., Ramsey G. H., Ponder W. H., Abbott J. H., Hamel L. E. and Kariher P. H. (1993). J. Air Waste Manage. Assoc., **43**, 242-247, 1993.
3. Yamamoto T. and Futamura S. (1998). Combust. Sci. Technol., **133**, 117-133, 1998.
4. Sobacchi M. G., Saveliev A. V., Fridman A. A., Gutsol A. F. and Kennedy L. A., Plasma Chem. Plasma Process., **23**, 347-370, 2003.
5. Ogata A., Ito D., Mizuno K., Kushiyama S., Gal A. and Yamamoto T. (2002). Appl. Catal. A-Gen., **236**, 9-15, 2002.
6. Park D.W., Yoon S.H., Kim G.J. and Sekiguchi H., (2002). J. Ind. Eng. Chem. **8**, 393-398 2002.
7. Oda T., Yamashita R., Haga I., Takahashi T. and Masuda S. (1996). IEEE Trans. Ind. Applicat., **32**, 118-124, 1996.
8. Oh S.M., Kim H.H., Ogata A., Einaga H., Futamura S. and Park D.W. (2005). Catal. Lett., **99**, 101-104, 2005.
9. Futamura S., Einaga H., Kabashima H. and Lee Y. H.(2004). Catal. Today, **89**, 89-95, 2004.
10. Kim H.H., Oh S.M., Ogata A. and S. Futamura (2004). Cataly. Lett., **96**, 189-194, 2004.
11. Ogata, A. Einaga H., Kabashima H., Futamura S., Kushiyama S. and Kim H.H. (2003). Appl. Catal. B-Environ., **46**, 87-95, 2003.
12. Ogata A., Ito D., Mizuno K., Kushiyama and S., Yamamoto T. (2001). IEEE Trans. Ind. Applicat., **37**, 959-964, 2001.
13. Oh S.M., Kim H.H., Einaga H., Ogata A., Futamura S. and Park D.W.(2006), Thin Solid Films, in press.
14. Suzuki I., Namba S. and Yashima T. (1983). J. Catal., **81**, 485-488, 1983.
15. Hara N. and Takahashi H., Eds. (1975). "Zeolite – Kiso to Ohyo (in japanese)", Tokyo,

Japan, Kodansya Scientific, p.103, 1975.

16. Kawazoe K., Kawai T. and Takeguchi Y. (1966). Seisan Ken-Kyu (in japanese), **18** 181-185, 1966.
17. Einaga H., Ibusuki T. and Futamura S. (2001). IEEE Trans. Ind. Applicat., **37**, 1476-1482, 2001.