Catalysis Letters 38 (1996) 21–25

Reaction of adsorbates derived from cyanuric acid on a Cu-MFI zeolite with nitrogen oxide and oxygen

Hiroshi Takeda and Masakazu Iwamoto [1]

Catalysis Research Center, Hokkaido University, Sapporo 060, Japan

Received 23 October 1995; accepted 8 December 1995

The reaction of adsorbates derived from cyanuric acid on a Cu-MFI zeolite with NO_x and O_2 has been studied by a pulse technique. The formation rate of N_2 in the NO_x or $NO_x + O_2$ pulse experiments on a cyanuric acid-preadsorbed Cu-MFI zeolite was much higher than that in the O_2 pulse system, indicating that the reactivity of the adsorbates with NO_x is much higher than with O_2. The product distribution in the first five pulses was greatly changed by the presence of water but the summed product distributions were the same. The formation of surface NH_3 or its derivatives during the reaction of NO and O_2 on cyanuric acid-preadsorbed Cu-MFI in the presence of H_2O is postulated.

Keywords: Cu-MFI catalyst; selective catalytic reduction of NO; cyanuric acid; isocyanic acid; isocyanate species; pulse technique

1. Introduction

The clarification of the reaction mechanism of selective catalytic reduction of NO by hydrocarbons (SCR-HC) has been widely and eagerly studied due to the importance of the reaction for the settlement of air pollution and acid rain [1]. Major targets of the present mechanistic studies are to reveal (1) the initial or important step to reduce NO selectively [2–5], (2) the final intermediate which gives N_2 [3,5–9], and (3) the active sites or the role of metal ions and acid site [4,10]. Concerning the second question many investigators have reported that an isocyanate (–NCO) species was observed on the catalyst surface during the SCR-HC [5,7,8,11] and indeed the –NCO species reacted with NO or O_2 to produce N_2 [8]. On the other hand, it was also reported that the –NCO species was not formed when ineffective reductants (CO, CH_3OH) were used for the reduction of NO [8]. Although these observations suggest the –NCO species to be a possible intermediate to give N_2, several questions remain to be solved; for example, the preferential reactant among NO, NO_2, and O_2 toward the surface –NCO species, the reaction stoichiometry between the –NCO species and NO_x or O_2, and the effect of water vapor on the reactivity of the adsorbate.

In this study, the pyrolysis of cyanuric acid ($(HOCN)_3$) to isocyanic acid (HNCO) at 573 K [12] has been employed to obtain the surface active adsorbates on Cu-MFI:

$$(HOCN)_3 \xrightarrow[\geqslant 573\ K]{} 3HNCO$$

The reactivity of NO_x or O_2 to the adsorbates has been evaluated by a pulse technique. A great difference between the reactivity of NO and that of O_2 and an unexpected effect of water addition will be shown.

2. Experimental

The Cu-MFI catalyst used was the same as that reported previously [13]. The SiO_2/Al_2O_3 molar ratio and the exchange level of Cu^{2+} ion were 23.3 and 105%, respectively. Cu-MFI was pretreated at 773 K in a He flow for 4 h before the pulse experiment.

The pulse experiment was carried out at 573 K on 5 mg of Cu-MFI mounted in a microreactor. The reaction apparatus was similar to that of Choudhary et al. [14]. A constant stream of helium of 50 $cm^3\ min^{-1}$ (GHSV, 300000 h^{-1}) was employed as a carrier gas. An aqueous solution of cyanuric acid (90 μl, 11.6 mmol ℓ^{-1}) was five times introduced onto the catalyst bed at 573 K as a pulse in the He carrier. The total amount of cyanuric acid introduced was 1046 μmol g-cat^{-1}, but most ran from the catalyst bed and the deposited amount was 22–29 μmol g-cat^{-1} as described later. After the introduction of the cyanuric acid, either O_2 (10.0%), NO_x (1.0%), H_2O (4.1%), or a mixture of NO_x (1.0%) + O_2 (10.0%), or NO_x (1.0%) + O_2 (10.0%) + H_2O (4.1%) in He was pulsed onto the catalyst at 573 K. Pulse size and pulse length were 1.36 cm^3 (12.1 mmol g-cat^{-1}) and 1.63 s, respectively. After passing through the catalyst bed, the reactants and products were led to Porapak Q and Molecular Sieve 5A columns to separate N_2O, CO_2, O_2, N_2, and CO. The next pulse was then introduced in 20 min after the previous pulse.

---

[1] To whom correspondence should be addressed.

3. Results

3.1. Reaction of adsorbates derived from cyanuric acid with O_2, NO_x or $NO_x + O_2$

The amounts of products formed in the pulse experiments in the absence of water vapor are plotted as a function of the number of pulses in fig. 1. In the O_2 system, a small amount of N_2 (ca. 2 μmol g-cat^{-1} per pulse) was steadily formed during the 1st–19th pulses. In contrast, in the NO_x or $NO_x + O_2$ systems a lot of N_2 was formed at the initial stage, the rate of N_2 formation was steeply decreased, and no formation of N_2 was observed at the 5th pulse. The behavior of CO_2 formation was almost the same as that of N_2 formation in the corresponding pulse experiment as shown in fig. 1B.

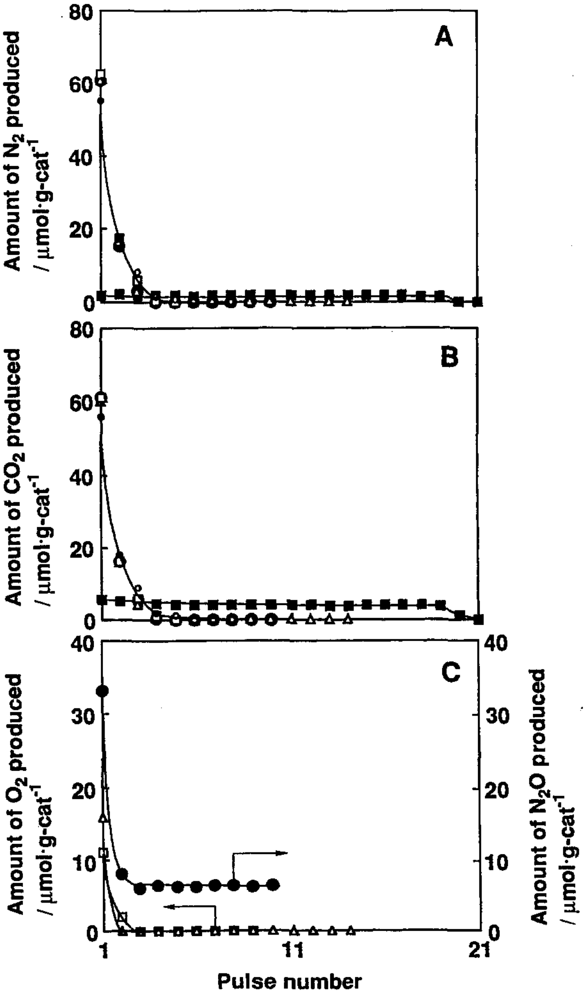

Fig. 1. Change in the formation rates of products with the gas composition introduced onto the cyanuric acid-preadsorbed Cu-MFI. The formation of O_2 or N_2O is observed in the NO_2-containing systems and the NO system, respectively. Amount of cyanuric acid introduced, 1046 μmol g-cat^{-1}; reaction temperature, 573 K; flow rate of carrier gas, 50 cm^3 min^{-1} (GHSV, 300000 h^{-1}); pulse size, 1.36 cm^3; pulse interval, 20 min. (■) O_2 (10.0%); (●) NO (1.0%); (△) NO_2 (1.0%); (○) NO (1.0%) + O_2 (10.0%); (□) NO_2 (1.0%) + O_2 (10.0%).

N_2O and O_2 were detected as products besides N_2 and CO_2. The formation of N_2O was observed only in the NO system (fig. 1C). It should be noted that a constant amount of N_2O was produced at the 3rd–10th pulses without any formation of N_2 and CO_2. The ratio of the amount of NO consumed to the amount of N_2O formed was approximately 3, suggesting that the disproportionation reaction ($3NO \rightarrow N_2O + NO_2$) proceeded on Cu-MFI. Indeed, the N_2O formation at this temperature has already been reported for the flow system[#1]. The amount of N_2O formed in the reaction with surface adsorbates was thus evaluated by the subtraction of the amount formed through the disproportionation from the total amount. In the NO_2 and $NO_2 + O_2$ systems, a small amount of O_2 was produced at the initial stage of pulse experiment as shown in fig. 1C.

After the reaction of fig. 1, that is, when the formation of N_2 and CO_2 was not observed any longer, the catalyst was heated to 773 K in an O_2 (1.0%) + He flow (TPO) to evaluate the amount of residue on the Cu-MFI sample. No formation of any products was observed in the TPO experiment, indicating that all adsorbates were reacted in the above pulse experiments.

The total amounts of products during the experiments of fig. 1 are summarized in table 1. The total amounts of N_2 generated in the NO_x-containing pulse systems were 83 ± 4 μmol g-cat^{-1}, which were approximately twice as much as that in the O_2 system. The total amounts of CO_2 formed were almost constant at 83 ± 3 μmol g-cat^{-1}. The amount of N_2 or CO_2 produced was only 2.5–2.7% of the cyanuric acid injected (1046 μmol g-cat^{-1}) during the adsorption treatment, indicating that most of cyanuric acid passed through the catalyst bed under the present adsorption conditions.

3.2. Pulse experiments in the presence of water vapor

To clarify the effect of water addition on the reactivity of the adsorbates derived from cyanuric acid, the $NO + O_2 + H_2O$ mixture was pulsed onto the adsorbates on Cu-MFI. The results are shown in fig. 2. The behavior of CO_2 formation was almost the same as that without H_2O (fig. 1B), while that of N_2 formation was quite different from that without H_2O (fig. 1A). The total amounts of CO_2 and N_2 formed are summarized in table 1.

Next, H_2O was first pulsed and then the mixture of NO and O_2 was used to reveal the cause of the remarkable effect of the water addition (fig. 3). Interestingly, in the H_2O pulses CO_2 alone was formed, without any formation of N_2, in a similar manner to that in fig. 2. N_2 formation was observed in the subsequent $NO + O_2$ pulses. The results are quantitatively shown in table 1.

[#1] The conversion level of NO to N_2O on a 143% exchanged Cu-MFI catalyst was 13% at T = 573 K, SV = 1800 h^{-1} and P_{NO} = 1.0% (in He) [15].

Table 1
Product distribution in the pulse experiments on cyanuric acid-preadsorbed Cu-MFI [a]

Gases pulsed	Product distribution / (μmol g-cat^{-1})				
	N_2	N_2O	CO_2	CO	O_2
O_2	34	0	82	0	−55 [b]
NO	79	43 [c]	84	0	0
NO_2	80	0	80	0	17
$NO + O_2$	83	0	86	0	− [d]
$NO_2 + O_2$	86	0	84	0	21
$NO + O_2 + H_2O$ [e]	69	0	75	0	− [d]
H_2O and then $NO + O_2$ [f]	0 (67 [g])	0 (0 [g])	73 (0 [g])	0 (0 [g])	0 (− [g,d])

[a] NO (NO_2) (1.0%), O_2 (10.0%), H_2O (4.1%); amount of cyanuric acid introduced, 1046 μmol g-cat^{-1}; catalyst weight, 5 mg; carrier gas flow rate, 50 cm^3 min^{-1} (GHSV, 300000 h^{-1}); temperature, 573 K; pulse size, 1.36 cm^3 (12.1 mmol g-cat^{-1}); pulse interval, 20 min.

[b] The amount of O_2 consumed.

[c] The contribution of disproportionation was subtracted from the total amount.

[d] The amount of O_2 consumed cannot be evaluated due to the NO_2 formation.

[e] The data from fig. 2.

[f] The data from fig. 3.

[g] The amount of products at the $NO + O_2$ pulses.

4. Discussion

4.1. *Surface reactions of adsorbates with NO_x and $NO_x + O_2$ in the absence of H_2O*

As has already been mentioned in the Introduction, cyanuric acid decomposes to yield isocyanic acid at 573 K. In addition, as will be described in the following discussion, the ratio of the amount of nitrogen to that of carbon in the products was approximately one in each pulse experiment. To confirm the adsorbed species we have applied an IR technique but complicated absorption bands have been observed, some of which were assignable to surface OH, CN, and NCO species and some remained unidentified. The surface adsorbate after the introduction of cyanuric acid has here been assumed to be in the form of HNCO.

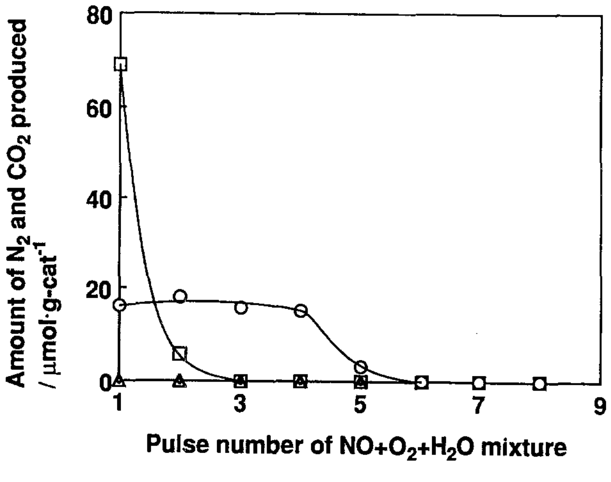

Fig. 2. Product distribution during the pulse experiment of $NO + O_2 + H_2O$ onto the cyanuric acid-preadsorbed Cu-MFI catalyst. NO (1.0%) + O_2 (10.0%) + H_2O (4.1%); the other experimental conditions are the same as those of fig. 1. (○) N_2; (△) N_2O; (□) CO_2; (◇) CO.

The formation rate of N_2 in the O_2 system was much lower than those in NO_x or $NO_x + O_2$ systems as shown in fig. 1. The profiles of N_2 formation in the $NO_x + O_2$ systems were almost the same as those in the NO_x systems. The results clearly reveal that the reactivity of the surface HNCO to NO_x is much higher than that to O_2 and the adsorbate reacts selectively with NO_x even in the presence of O_2.

In the O_2 system, the ratios of (amount of N_2 formed)/(amount of CO_2 formed) and (amount of O_2 consumed)/(amount of CO_2 formed) were 0.42 and 0.67, respectively. These values are close to $\frac{1}{2}$ and $\frac{3}{4}$, and indicate the progress of the following reaction:

$$HNCO + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + CO_2 + \tfrac{1}{2}H_2O \qquad (1)$$

Similar calculations suggest the following reactions for the NO, $NO + O_2$, and NO_2 ($+O_2$) systems.

$$HNCO + 2NO \rightarrow N_2 + \tfrac{1}{2}N_2O + CO_2 + \tfrac{1}{2}H_2O \qquad (2)$$

$$HNCO + NO + \tfrac{1}{4}O_2 \rightarrow N_2 + CO_2 + \tfrac{1}{2}H_2O \qquad (3)$$

$$HNCO + NO_2 \rightarrow N_2 + CO_2 + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \qquad (4)$$

In the $NO + O_2$ system, equimolar amounts of N_2 and CO_2 were produced without any formation of the other products. This indicates that the surface –NCO species reacted with NO selectively even in the presence of O_2 (reaction (3)). In the NO system, the unusual formation of N_2O was recognized in table 1. The amount of N_2O produced and the necessity of $\frac{1}{4}O_2$ in reaction (3) suggest a reaction, $NO \rightarrow \frac{1}{2}N_2O + \frac{1}{2}O$, and a subsequent reaction, $HNCO + NO + \frac{1}{2}O \rightarrow N_2 + CO_2 + \frac{1}{2}H_2O$.

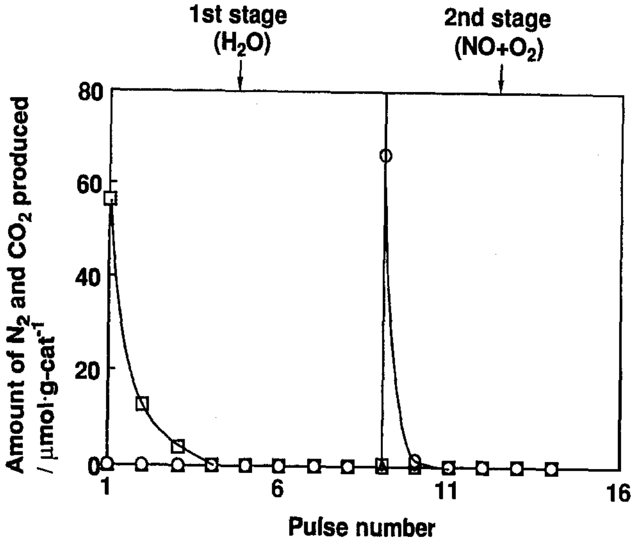

Fig. 3. Change in the formation profiles of products with the gas composition introduced onto the cyanuric acid-preadsorbed Cu-MFI catalyst. 1st stage, H_2O (4.1%); 2nd stage, NO (1.0%) + O_2 (10.0%); the other experimental conditions are the same as those of fig. 1. (○) N_2; (△) N_2O; (□) CO_2; (◇) CO.

The latter reaction is equal to reaction (3). After all, the reaction with NO proceeds as described in eq. (2).

The formation of O_2 is characteristic of the NO_2 and $NO_2 + O_2$ systems. The stoichiometry for the complete oxidation of HNCO with NO and oxygen can be expressed by eq. (3), though the active form of oxygen is unknown. Since there are two oxygen atoms in a NO_2 molecule, the excess oxygen has to be released in the form of O_2, which would be the reason for the formation of $\frac{1}{4}O_2$.

Similar pulse experiments and TPO experiments were carried out on a H-MFI zeolite and small amounts of N_2 and CO_2 (6 and 8 μmol g-cat^{-1}, respectively) were formed. It is clear that HNCO did not adsorb on the H-MFI zeolite and the copper ions are the active sites for the adsorption of HNCO.

4.2. Effect of water vapor on the surface reaction

The addition of H_2O into the $NO + O_2$ mixture greatly changed the formation rate of N_2 as shown in fig. 2. In addition, CO_2 and N_2 were separately formed in the H_2O and the subsequent $NO + O_2$ pulses, as shown in fig. 3. The amounts of CO_2 and N_2 produced in fig. 3 were approximately equal to those in fig. 2 and table 1. Although the reaction pathway should be studied in more detail, for example, by using an IR technique, we wish here to suggest one possibility.

Unland [16] has reported that the HNCO species reacts with water to yield CO_2 and NH_3 (eq. (5)). In addition, Mizumoto et al. [17] reported that the

$$HNCO + H_2O \rightarrow CO_2 + NH_{3(ad)} \qquad (5)$$

selective reduction of NO with NH_3 in the presence of O_2 (SCR-NH_3) is well catalyzed on a Cu-FAU zeolite and the reaction stoichiometry is described by

$$NH_{3(ad)} + NO + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (6)$$

The same reaction has been reported to proceed on Cu-MOR [18], Cu-MFI [19], H-MOR [20] and H-MFI [21] catalysts. On the basis of figs. 2 and 3 and these reports, it is possible that the reactions (5) and (6) proceed continuously on Cu-MFI in the presence of water. The net reaction can be described by reaction (3). The confirmation of the surface NH_3 adsorbates should be carried out in the future study.

Another possibility to explain the results is the formation of hydrated Cu^{2+} cations. Mizumoto et al. [17] have observed that the reduction rate of NO in the SCR-NH_3 became slow upon the addition of H_2O, and concluded that the competitive adsorption of H_2O on Cu^{2+} cations lowered the reaction rate on the basis of the kinetic study. In the present study there is a possibility that the hydration of Cu^{2+} cations affects the reaction rates.

5. Conclusions

It was clarified that the adsorbates derived from cyanuric acid react with NO_x selectively even in the presence of O_2. In addition, it follows that water vapor does not affect the product distribution in the reaction of HNCO with a mixture of $NO + O_2$, though the reaction rates were greatly changed.

Acknowledgement

The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

[1] M. Iwamoto and N. Mizuno, J. Automobile Eng. 207 (1993) 23.
[2] J.O. Petunchi and W.K. Hall, Appl. Catal. B 2 (1993) L17;
M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett. 26 (1994) 277;
T. Tabata, H. Ohtsuka, M. Kokitsu and O. Okada, Bull. Chem. Soc. Jpn. 68 (1995) 1905;
Y. Nishizaka and M. Misono, Chem. Lett. (1994) 2237.
[3] T. Tanaka, T. Okuhara and N. Misono, Appl. Catal. B 4 (1994) L1;
K.A. Bethke, C. Li, M.C. Kung, B. Yang and H.H. Kung, Catal. Lett. 31 (1995) 287.
[4] R. Burch and S. Scire, Appl. Catal. B 3 (1994) 295;
T. Inui, S. Iwamoto, S. Kojo, S. Shimizu and T. Hirabayashi, Catal. Today 22 (1994) 41;
E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73;
C. Yokoyama and M. Misono, Catal. Today 22 (1994) 59.

[5] C. Yokoyama and N. Misono, J. Catal. 150 (1994) 9.
[6] N.W. Hayes, W. Grünert, G.J. Huchings, R.W. Joyner and E.S. Shpiro, J. Chem. Soc. Chem. Commun. (1994) 531.
[7] F. Poignant, J. Saussey, J.C. Lavalley and G. Mabilon, J. Chem. Soc. Chem. Commun. (1994) 89;
G.R. Banwenda, A. Obuchi, A. Ogata and K. Mizuno, Chem. Lett. (1994) 2109;
G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno and J. Skrzypek, Appl. Catal. B 6 (1995) 311.
[8] Y. Ukisu, S. Sato, G. Muramatu and K. Yoshida, Catal. Lett. 16 (1992) 11;
H. Yahiro, Y. Yu-u, H. Takeda, N. Mizuno and M. Iwamoto, Shokubai 35 (1993) 130;
C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, J. Chem. Soc. Chem. Commun. (1995) 813.
[9] B.L. Yang, M.C. Kung, H.H. Kung, B.W. Jang and J.J. Spivey, Paper 83e presented at the 1994 AIChE Annual Meeting, San Francisco, November 1994.
[10] Y. Li and J.N. Armor, J. Catal. 145 (1994) 1;
A. Satsuma, K. Yamada, T. Mori, M. Niwa, T. Hattori and Y. Murakami, Catal. Lett. 31 (1995) 367;
J.O. Petunchi and W.K. Hall, Appl. Catal. B 3 (1994) 239;
W. Grünert, N.W. Heyes, R.W. Joyner, E.S. Shpiro, M.R.H. Siddiqui and G. Baeva, J. Phys. Chem. 98 (1994) 10832;
A.V. Kucherov, J.L. Gerlock, H-W. Jen and M. Shelef, J. Catal. 152 (1995) 63.
[11] V.A. Bell, J.S. Feeley, M. Deeba and R.J. Farrauto, Catal. Lett. 29 (1994) 15;
F. Radtke, R.A. Koeppel and A. Baiker, J. Chem. Soc. Chem. Commun. (1995) 427;
F. Solymosi and T. Bánsági, J. Catal. 156 (1995) 75.
[12] G. Herzberg and C. Reid, Discussions Faraday Soc. 9 (1952) 92.
[13] M. Iwamoto and H. Takeda, Catal. Today, in press.
[14] V.R. Choudhary, S.D. Sansare, A.M. Rajput and D.B. Akolekar, Appl. Catal. 69 (1991) 187.
[15] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa, J. Phys. Chem. 95 (1991) 3727.
[16] M.L. Unland, J. Catal. 31 (1973) 459.
[17] M. Mizumoto, N. Yamazoe and T. Seiyama, J. Catal. 59 (1979) 319.
[18] J.G.M. Brandin, L.A.H. Anderson and C.U.I. Odenbrand, Catal. Today 4 (1989) 187.
[19] T. Komatu, N. Nunokawa, I.S. Moon, T. Takahara, S. Namba and T. Yashima, J. Catal. 148 (1994) 427;
T. Komatu, T. Ogawa and T. Yashima, J. Phys. Chem. 99 (1995) 13055.
[20] E.Y. Choi, I.-S. Nam, Y.G. Kim, J.S. Chung, J.S. Lee and M. Nomura, J. Mol. Catal. 69 (1991) 247.
[21] I.S. Moon, S. Namba and T. Yashima, Sekiyu Gakkaisi 36 (1993) 339.