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Liquid-phase methanol carbonylation catalyzed over tin promoted nickel–aluminium layered double hydroxide

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Abstract

A nickel–aluminum layered double hydroxide (LDH), of which structure is similar to that of hydrotalcite, has been synthesized. Liquid-phase carbonylation of methanol to methyl acetate is catalyzed over the LDH in presence of methyl iodide at 473 K. Dimethyl ether is also formed in the reaction, but formation of acetic acid is undetectable. Nickel ions in the LDH can be replaced with tin ions, and the presence of tin significantly promotes the activity of the LDH. Formation of methyl formate depends on the pressure of carbon monoxide in the reaction, suggesting that insertion of carbon monoxide to methyl iodide is a key step of the carbonylation and dimethyl ether reacts with the intermediate to form methyl formate.

Keywords: Methanol carbonylation; Hydrotalcite-like structure; Methyl acetate; Dimethyl ether

1. Introduction

Methanol carbonylation is one of the most important reactions for the manufacture of acetic acid and methyl acetate, which is further carbonylated to acetic anhydride. The reaction was first practiced in a high temperature (573 K) and pressure (68 MPa) process using boron trifluoride or phosphoric acid [1]. A metal carbonyl catalyst was discovered by Reppe, but the process still required pressure above 50 MPa [2,3]. The first commercial process was developed by BASF. In the process the cobalt carbonyl catalyst was used in presence of methyl iodide at 523 K and 68 MPa [4]. A breakthrough was made by discovery of the rhodium carbonyl catalyst developed by Monsanto [5,6]. However, this well-known synthetic route of methanol carbonylation still suffers from recovery of expensive rhodium metal, multiple steps, complicated synthetic operations and lengthy work-up procedures. Attempts have been made to use heterogeneous catalysts for methanol carbonylation [7], because the system will be advantageous in separation and recovery of the products and recycling of the catalysts. A number of supported rhodium catalysts are reported to be active under vapor-phase conditions [8–13]. Hydrotalcite, $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2}$, is known as a layered double hydroxide (LDH) in which a wide variety of metal cations can be introduced [14]. The material is a good support of rhodium for the liquid-phase reaction [15]. LDH consists of positively charged brucite-like layers with charge-balancing anions and water molecules and generally represented by the formula of ${M_{1-x}}^{2+}{M_x}^{3+}(OH)_2(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} is a divalent cation, e.g., Mg, Ni, or Zn; M^{3+} is a trivalent cation, e.g., Al, Cr or Fe; and A^{n-} is a charge compensating anion such as ${CO_3}^{2-}$, ${NO_3}^{-}$, etc. Nickel is another active metal for methanol carbonylation [16–18] and Fujimoto et al. showed that solid-phase nickel catalysts can catalyze vapor-phase carbonylation of methanol to methyl acetate [19]. Thus, LDH containing Ni^{2+} is a candidate of the catalyst for methanol carbonylation. In this paper we will show that LDH whose cations are nickel and aluminum can catalyze liquid-phase methanol carbonylation in presence of methyl iodide and addition of tin to the solid promotes the activity.

2. Experimental

$Ni_{0.75}Al_{0.25}$ LDH was synthesized by a coprecipitation technique at room temperature. An aqueous solution of $Ni(NO_3)_2$ and $Al(NO_3)_3$ was mixed with an aqueous

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solution of Na_2CO_3 (0.3 M) and NaOH (2–3 M) at pH 10. The resulting mixture was stirred for 2 h at room temperature and aged at 343 K for 3 h. The precipitate was filtered, washed and dried at 373 K for 24 h. Samples containing tin, $(Ni_{1-n}Sn_n)_{1-x}Al_x$ LDH ($0 < n < 0.5$, $0.2 = x < 0.5$), was prepared by the same procedure as above except the presence of $SnCl_4$ in the starting solution.

Patterns of powder X-ray diffraction (XRD) of the samples were recorded with a Rigaku Rotaflex using nickel-filtered Cu Kα.

The BET surface areas of the samples were determined from nitrogen physisorption isotherms.

Temperature-programmed reduction (TPR) of the samples (0.10 g) was carried out in a stream of 5 vol.% of hydrogen diluted with argon at a flow rate of 1.8 $dm^3\ h^{-1}$. Temperature of the sample bed was risen linearly at a rate of 300 $K\,h^{-1}$. The hydrogen consumption was regularly monitored with a thermal conductivity detector (TCD).

Catalytic tests were performed in an autoclave (0.2 dm^3). Prior to the reaction the catalyst (0.20 g) was stabilized under evacuation followed by reduction with hydrogen at 473 K for 2 h and sealed in a glass capsule. In a typical experiment, the capsule was placed in the reactor with mixture of methanol (780 mmol) and methyl iodide (35 mmol), and CO (101 mmol) was introduced at 1.2 MPa after displacing air inside of the reactor with argon. The capsule was broken by pressurizing and the reactor was heated up to 473 K. The products were analyzed with an Ohkura-802 gas chromatograph (TCD) whose columns were PEG 1500 (2 m) and Porapak T (2 m).

3. Results and discussion

3.1. XRD characterization

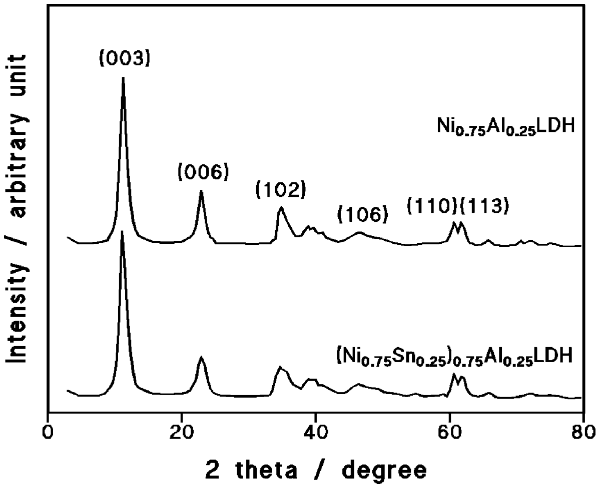

Fig. 1. XRD patterns of $Ni_{0.75}Al_{0.25}$ LDH and $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH.

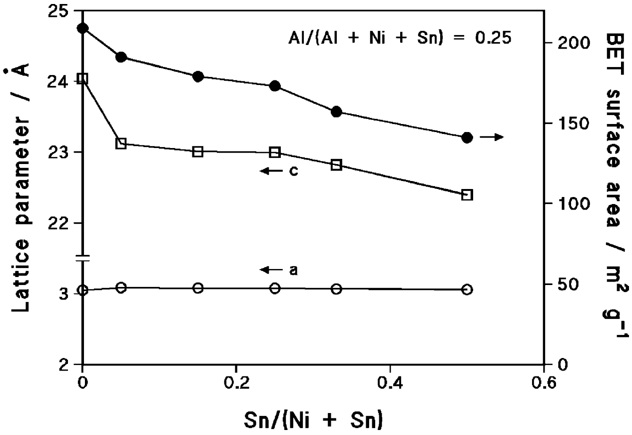

Fig. 2. Lattice parameters and BET surface area of $(Ni_{1-n}Sn_n)_{0.75}Al_{0.25}$ LDH.

The XRD pattern of $Ni_{0.75}Al_{0.25}$ LDH showed that the sample has hydrotalcite-like structure with good crystallinity (Fig. 1) [15]. The peaks at 11° and 22° in 2θ can be attributed to (0 0 3) and (0 0 6) of rhombohedral symmetry, respectively, and the values depend on the lattice parameter, *c*, corresponding to three times thickness of the brucite-like layer. The peaks were broad in the patterns of $(Ni_{1-n}Sn_n)_{1-x}Al_x$ LDH (see Fig. 1), suggesting that the distance between the layers are somehow disordered compared with $Ni_{0.75}Al_{0.25}$ LDH. The lattice parameter, *a*, corresponding to the average distance of cations in the positive brucite-like layers, was almost the same regardless of the Sn content in the samples (Fig. 2). This shows that Sn^{4+} is replaced with Ni^{2+} in the positive brucite-like layers, whereas the ionic radii of Ni^{2+} and Sn^{4+} are the same (0.83 Å). The increase in Sn^{4+} ions in the positive layers results in an increase in the charge of the layers causing stronger electrostatic interaction between the positive layers and the negative inter-layers. The interaction can account for the decrease in the value of "*c*" with an increase in the number of Sn^{4+} while an increase in the number of $CO_3{}^{2-}$ ions may affect the change in the distance (see Fig. 2). The similar tendency was observed by changing the value of *x*, i.e., Al/(Al + Ni + Sn) (Fig. 3). The higher content of Al^{3+} in the positive layers will result in the stronger

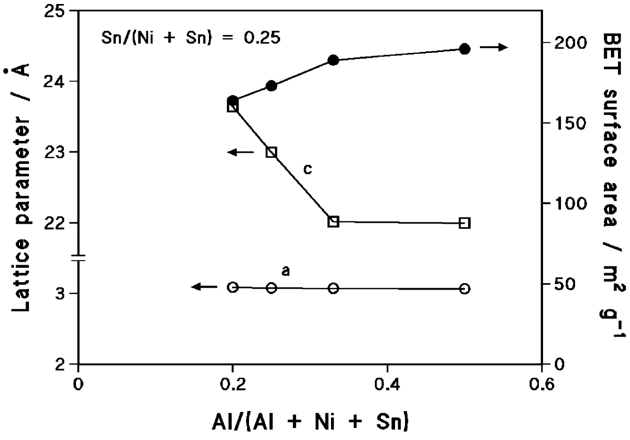

Fig. 3. Lattice parameters and BET surface area of $(Ni_{0.75}Sn_{0.25})_{1-x}Al_x$ LDH.

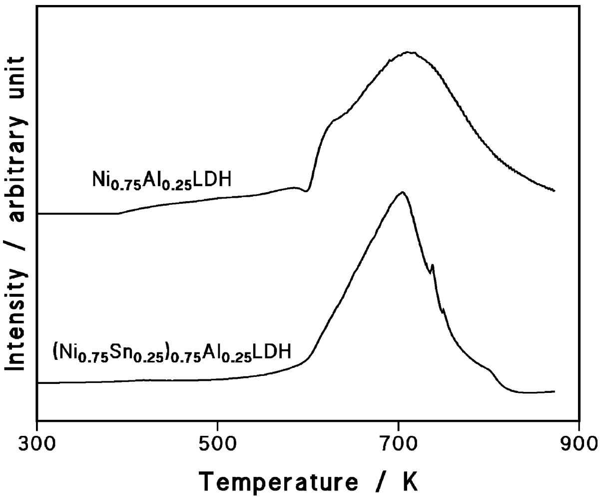

Fig. 4. TPR profiles of $Ni_{0.75}Al_{0.25}$ LDH and $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH.

electrostatic bonding between the layers. The BET surface areas of the samples were as high as 141–209 $m^2\,g^{-1}$. It decreased with an increase in Sn/(Ni + Sn), but increased with an increase in Al/(Al + Ni + Sn) (see Figs. 2 and 3).

3.2. Temperature-programmed reduction

The TPR profiles for $Ni_{0.75}Al_{0.25}$ LDH and $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH showed that slight hydrogen consumption takes place above ca. 400 K, while the major reduction peaks started from ca. 600 K (Fig. 4). The XRD patterns of these samples after reduction with hydrogen at 573 K for 1 h were very similar to those of the samples as prepared (see Fig. 1), appearing that the major part of nickel ions were retained in the structure. However, complete destruction of the LDH structure after the reduction at 773 K was confirmed by the XRD measurement.

3.3. Methanol carbonylation

Liquid-phase methanol carbonylation was catalyzed over $Ni_{0.75}Al_{0.25}$ LDH at 473 K. The major products were methyl acetate (MeOAc) and dimethyl ether (DME) without any loss of methyl iodide. A small amount of acetaldehyde (0.2 mmol or less for 12 h) was by-produced, but no formation of acetic acid was detected. Addition of tin to the catalyst increased the yield of MeOAc (Fig. 5). The maximum yield of 32.3 mmol was produced with $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH in the reaction for 12 h. The total methanol conversion was almost stable up to n, i.e., Sn/(Ni + Sn), equal to 0.25, but decreased at the higher value. When the value of $1 - x$, i.e., (Ni + Sn)/(Al + Ni + Sn), was changed, the methanol conversion and the yield of MeOAc increased with an increase in the value of $1 - x$, but they decreased at $1 - x$ being equal to 0.8 (Fig. 6).

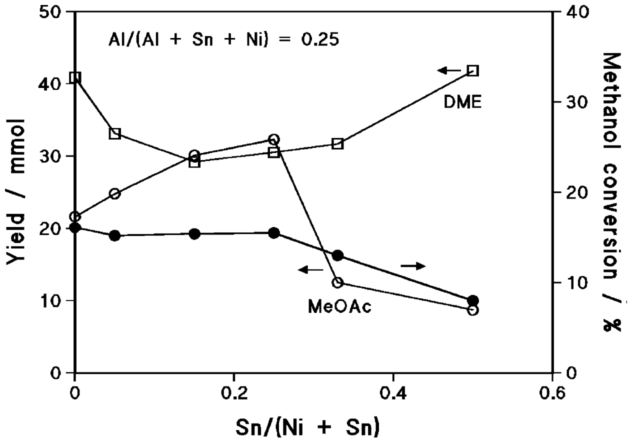

Fig. 5. Catalytic activity of $(Ni_{1-n}Sn_n)_{0.75}Al_{0.25}$ LDH in liquid-phase methanol carbonylation at 473 K for 12 h.

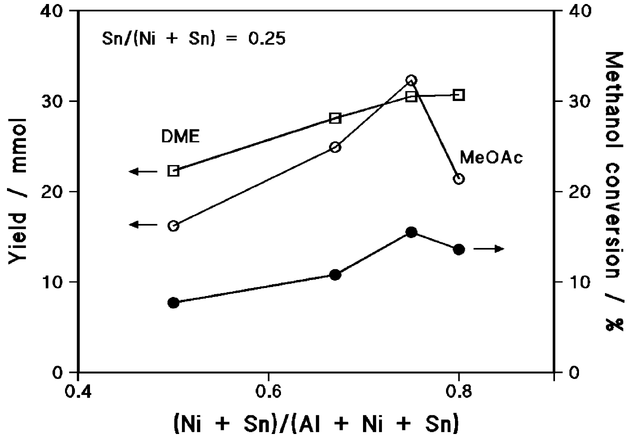

Fig. 6. Catalytic activity of $(Ni_{0.75}Sn_{0.25})_{1-x}Al_x$ LDH in liquid-phase methanol carbonylation at 473 K for 12 h.

In the initial stage of the reaction with $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH, production of MeOAc was small and it was accelerated with a time period of reaction (Fig. 7). The XRD pattern of the catalyst recovered in air after the reaction for 12 h was very similar to that prior to the reaction. The activity of the recovered catalyst without the pretreatment with

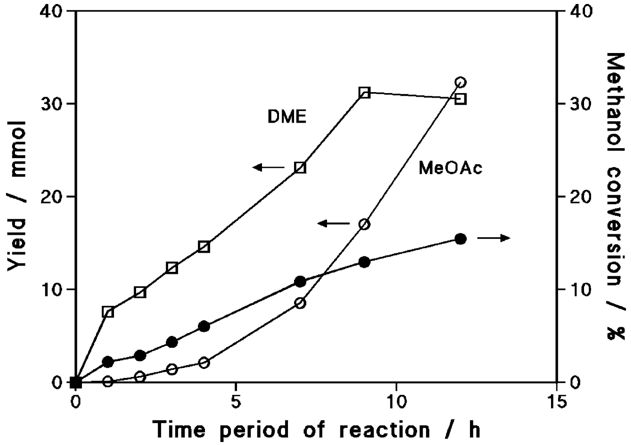

Fig. 7. Time profile of liquid-phase methanol carbonylation over $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH at 473 K.

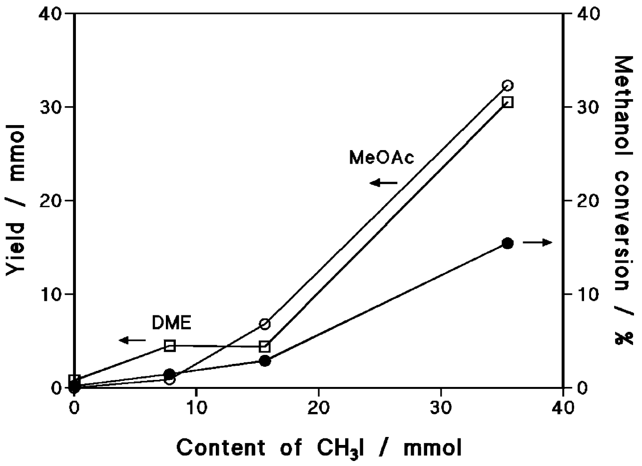

Fig. 8. Effect of CH_3I concentration on liquid-phase methanol carbonylation over $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH at 473 K for 12 h.

hydrogen at 473 K was almost half of the new one. We did not carry out the pretreatment in this experiment because organic compounds strongly stuck on the recovered catalyst. Nevertheless, the reaction was repeatable with the recovered catalyst, showing that the methanol carbonylation takes place on the LDH catalyst. Since a catalyst of 5 wt.% Ni and 5 wt.% Sn supported on alumina produced only 6 mmol of methyl acetate for 12 h, the structure of LDH strongly affects its catalytic activity.

No methanol carbonylation occurred in the absence of methyl iodide except for formation of a small amount of DME. Hence, methanol cannot be directly carbonylated over the catalyst, and the presence of methyl iodide is essential in the formation of MeOAc. The yield of MeOAc depended on the content of methyl iodide (Fig. 8). The production of MeOAc also depended on the CO pressure (Fig. 9). Thus, the reaction step

$$CH_3I + CO \rightarrow CH_3COI,$$

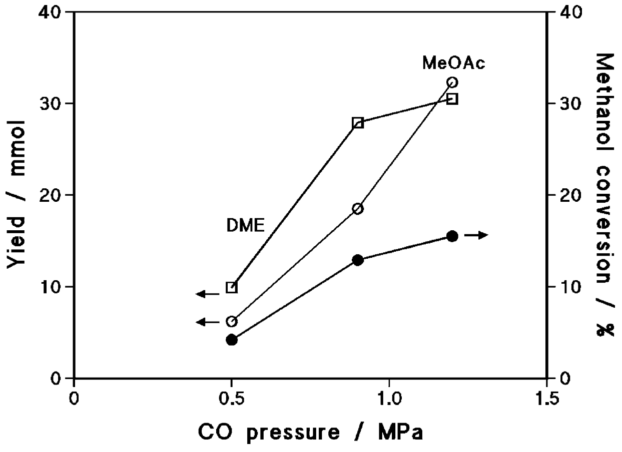

Fig. 9. Effect of CO pressure on liquid-phase methanol carbonylation over $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH at 473 K for 12 h.

which is generally accepted in the reaction scheme of methanol carbonylation [7,18], is probably the key step in the reaction over the LDH, indicating that actual reactant is not methanol but methyl iodide, which is reproduced in the reaction. Nickel carbonyl complex would catalyze the reaction step [17,18], but it is known that the activity is small in absence of promoters such as phosphine and tin organic compounds. In addition XRD pattern of $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH recovered after the reaction showed no change in the structure, appearing that dissolution of nickel into the solvent hardly takes place. Shikada et al. pointed out the importance of valence shift between Ni^0 and Ni^{2+} to produce I^- and CH_3–Ni to which CO is inserted [20]. The activity of the LDH catalysts was not stable without the pretreatment with hydrogen, suggesting that partial reduction of nickel is an important step in the catalytic process. However, no peak attributed to nickel metal was recorded in the XRD pattern of $(Ni_{0.75}Sn_{0.25})_{0.75}Al_{0.25}$ LDH after the reaction. The function of Sn^{4+} to the reaction is not clear at present. The cations may stabilize the active species, but the excessive addition of Sn^{4+} causes a decrease in the quantity of the active nickel species (see Fig. 5). A decrease in the number of Al^{3+} ions in the positive layers corresponds to an increase in the number of nickel ions (see Fig. 6); however, the activity decreases when the number of Al^{3+} ions is too small, suggesting that presence of Al^{3+} also contributes to the activity of the nickel species.

In the reaction,

$$CH_3I + CH_3OH \rightarrow DME + HI$$

would take place [17], but the lower pressure of carbon monoxide resulted in the less formation of DME (see Fig. 7), showing that the interaction between methyl iodide and methanol to form DME is small. Reaction between CH_3COI and methanol results in formation of MeOAc, that is [13],

$$CH_3OH + CH_3COI \rightarrow MeOAc + HI.$$

The reaction produces HI, which can catalyze dehydration of methanol to DME, and it accounts for the contribution of CO pressure to the formation of DME (see Fig. 7). Regeneration of methyl iodide will take place in the reaction of [17]

$$CH_3OH + HI \rightarrow CH_3I + H_2O.$$

However, formation of MeOAc is not linear to the concentration of methyl iodide or CO pressure (see Figs. 7 and 8), suggesting presence of other reaction route. Since the yield of DME at 12 h was smaller than that at 9 h (see Fig. 7), DME was also consumed in the reaction. Carbonylation of DME to MeOAc has been proposed in the vapor-phase reaction [19], and in actual, Shikada et al. showed that the reaction takes place over nickel supported on activated carbon [20,21]. Thus, CH_3COI reacts rather with DME than with methanol, that is,

$$CH_3COI + DME \rightarrow MeOAc + CH_3I,$$

and this can account for the induction period of formation of MeOAc (see Fig. 6).

References

[1] F.J. Weymouth, A.F. Millidge, Chem. Ind. (1966) 887.
[2] W. Reppe, US Patent 2 727 651 (1956).
[3] W. Reppe, US Patent 2 789 137 (1957).
[4] N. Kutenpov, W. Himmele, H. Hohenshutz, Hydrocarb. Process. 45 (1966) 141.
[5] F.E. Paulik, A. Hershman, W.R. Knox, J.F. Roth, US Patent 3 769 329 (1973).
[6] F.E. Paulik, A. Hershman, J.F. Roth, J.C.S. Chem. Commun. (1968) 1578.
[7] M.J. Howard, M.D. Jones, M.S. Roberts, S.A. Taylor, Catal. Today 18 (1993) 2271.
[8] T. Yashima, Y. Orikasa, N. Takahashi, N. Hara, J. Catal. 59 (1979) 53.
[9] N. Takahashi, Y. Orikasa, T. Yashima, J. Catal. 59 (1979) 61.
[10] A. Krywicki, M. Marczewski, J. Mol. Catal. 6 (1979) 431.
[11] N. De Blasio, E. Tempesti, A. Kaddouri, C. Mazzocchia, D.J. Cole-Hamilton, J. Catal. 176 (1998) 253.
[12] A.S. Merrenov, M.A. Abraham, Catal. Today 40 (1998) 397.
[13] H. Jiang, Z. Liu, P. Pan, G. Yuan, J. Mol. Catal. A 148 (1999) 215.
[14] R. Allmann, Acta Crystallogr. B 24 (1968) 972.
[15] M.P. Kapoor, Y. Matsumura, J.C.S. Chem. Commun. (2000) 95.
[16] R.F. Heck, J. Am. Chem. Soc. 85 (1963) 2013.
[17] N. Rizklla, in: D.R. Fahey (Ed.), Industrial Chemicals via C1 Processes, American Chemical Society, Washington, DC, 1987, p. 61.
[18] W.R. Moser, B.J. Marshik-Guerts, S.J. Okarasinski, J. Mol. Catal. A 143 (1999) 57.
[19] K. Fujimoto, K. Omata, T. Shikada, H. Tominaga, in: D.R. Fahey (Ed.), Industrial Chemicals via C1 Processes, American Chemical Society, Washington, DC, 1987, p. 208.
[20] T. Shikada, K. Fujimoto, H. Tominaga, in: D.R. Fahey (Ed.), Industrial Chemicals via C1 Processes, American Chemical Society, Washington, DC, 1987, p. 176.
[21] T. Shikada, K. Fujimoto, M. Miyauchi, H. Tominaga, Appl. Catal. 7 (1983) 361.