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Methanol dehydrogenation in the liquid phase with Cu-based solid catalysts

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Studies of methanol dehydrogenation in the liquid phase with Cu-based solid catalysts have shown (i) the product (methylal) is totally different from that in the gas–solid phase reaction (methyl formate) even using the same catalyst, and (ii) the differences in the calcination atmosphere of the catalyst (N_2 versus dry air) have a marked effect on the product selectivity (methylal versus methyl formate). These results are in contrast to the gas-phase reaction (commonly methyl formate). The results are discussed on the basis of surface species characterized with XPS and XRD.

Keywords: Methanol dehydrogenation; copper catalyst; slurry catalyst

1. Introduction

There have been reports concerning the Cu-based solid catalysts for the dehydrogenation of methanol to methyl formate in the gas–solid phase reaction [1–11],

$$2CH_3OH \rightarrow HCOOCH_3 + 2H_2 . \qquad (1)$$

To our knowledge, however, no attempts have been made to use the catalyst in the liquid phase (slurry catalyst), although there are several advantages of the liquid-phase reaction over the conventional gas-phase process [12]. We report here that the product distribution can be different between the reaction phases even using the same catalyst, and that the selectivity differs according to the method of catalyst preparation.

2. Experimental

2.1. CATALYST PREPARATION

All chemicals used were reagent grade. Cu–ZnO/SiO_2 was prepared modifying

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the method of ref. [1]. $Cu(CH_3COO)_2 \cdot H_2O$ (200 g), $ZnCO_3$ (15 g) (atomic ratio, Cu : Zn = 8.4 : 1), SiO_2 (Kanto Chemical Co., Inc., 10 g) and H_2O (80 ml) were mixed for 3 h and dried at 80°C for 8 h in a slow stream of Ar. The mixture was calcined in an alumina boat at 650°C for 3 h in a stream (300 ml/min) of N_2 (catalyst **a**) or dry air (catalyst **b**). $CuO–Cr_2O_3/SiO_2$ (catalyst **c**) was prepared by the literature method [2]. The BET specific surface areas of the catalysts were 32 m^2/g (catalyst **a**), 6.9 m^2/g (catalyst **b**) and 100 m^2/g (catalyst **c**), respectively, as determined by N_2 adsorption at −196°C.

2.2. REACTION OF METHANOL

Methanol was dried over CaH_2 and Na (twice) before use. The gas–solid catalytic reactions were performed using a conventional pulse reactor. The catalyst (100 mg) was loaded in the microreactor and pretreated in a He stream (25 ml/min) at 200°C for 3 h. After the treatment, 1.0 μl of methanol (degassed with He bubbling) was injected. The reaction temperature was 200°C, and the flow rate of the He carrier was maintained at 25 ml/min. The products were analyzed by gas chromatography (TCEP (1,2,3-tricyano(2-ethoxy)propane) column).

For the liquid-phase reactions, a stainless-steel autoclave was used. The Cu-containing catalyst (1.0 g) and methanol (150 ml) were charged under an Ar atmosphere, and suspended by stirring with a stainless-steel propeller (75 rpm). The autoclave was heated up to 200°C. The time taken to reach this temperature was about 1 h. At this temperature, the internal pressure was about 40 atm. For the analysis of reaction products, microsamples were withdrawn from the reaction mixture at appropriate time intervals through a stainless-steel inner sleeve equipped with an external condenser. The gas-phase sample was collected in a glass Schlenk tube after the reaction. The products in the liquid phase were analyzed quantitatively by gas chromatography (TCEP and PEG-6000 columns). CH_4, CO and CO_2 were analyzed by gas chromatography (active-carbon column), where a methane converter was used for the sake of precision. Preliminary runs carried out with different amounts of catalysts and stirring rates showed the absence of external diffusional limitations.

2.3. XPS AND XRD SPECTRA

XPS spectra were recorded with an Al K_α X-ray irradiation (1486.6 eV) at about 10^{-7} Torr. The samples were fixed on the double-sided adhesive tape. Binding energy was calibrated using the ubiquitous carbon C_{1s} peak at 284.6 eV.

XRD analyses were made with Rigaku, RAD-B system. Samples were ground under an Ar atmosphere, and packed as a thin layer into a shallow sample holder backed with a glass slide. Samples were scanned using a Mo K_α irradiation (0.70926 Å) at a rate of 1°C/min. Peaks were assigned by comparing the spectra with those of standard samples (Cu, Cu_2O and CuO).

3. Results and discussion

3.1. GAS-PHASE CATALYTIC REACTIONS

Fig. 1 shows the results for the pulse reactions with the three types of catalysts **a**–**c**. In each case, the single product was methyl formate. The observed high selectivity to methyl formate is consistent with the results obtained with a flow reactor system [1,2]. The lower activity of catalyst **b** than catalysts **a** and **c** may be attributable to its small specific surface area.

3.2. LIQUID-PHASE CATALYTIC REACTIONS

Fig. 2 shows the time courses of the product formation in the liquid phase with catalysts **a**–**c**. In all cases, no induction period was observed. In the gas phase, H_2 with trace amounts ($<0.1\%$) of CO, CH_4 and CO_2 was detected after the reaction, and excellent stoichiometries were obtained between H_2 and the sum of the dehydrogenated products for all the cases. From fig. 2, it is obvious that the selectivity is markedly different among the catalysts **a**–**c**. Namely, catalyst **a** (fig. 2a) gave methylal with 100% selectivity (methyl formate was not detected), while methyl formate was formed with $>99\%$ selectivity for catalyst **b** (fig. 2b). Catalyst **c** (fig. 2c) also dehydrogenated methanol into methyl formate with 100% selectivity.

The selectivity in the liquid-phase reaction is quite interesting on the following two points. (i) With regard to catalyst **a**, the product in the liquid-phase reaction (methylal) is totally different from that obtained in the gas-phase reaction (methyl formate). (ii) As observed for catalysts **a** and **b** the difference in the atmosphere during catalyst calcination affects the selectivity (methylal for catalyst **a** (N_2) and methyl formate for catalyst **b** (dry air)).

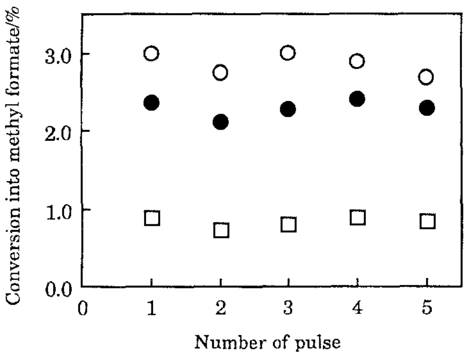


Fig. 1. Dehydrogenation of methanol in the gas–solid phase reaction with catalysts **a** (○), **b** (□) and c (●).

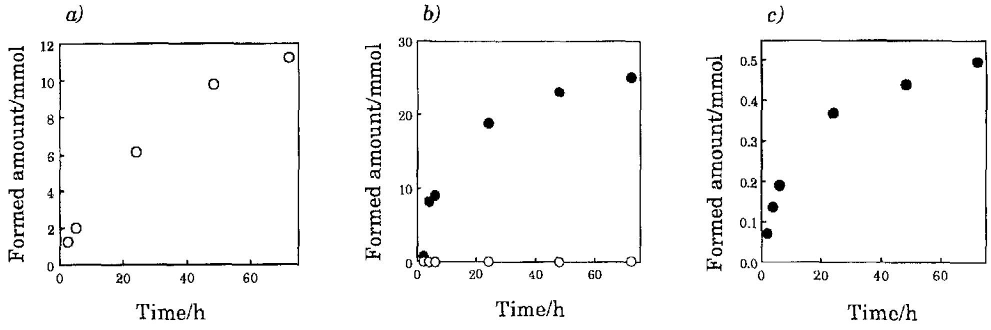


Fig. 2. Methylal (○) and methyl formate (●) formation from methanol in the liquid-phase reaction with catalysts **a** (a), **b** (b) and **c** (c).

3.3. NATURE OF THE CATALYST SURFACES

The observed peaks in the XPS spectra for catalysts **a** and **b** are summarized in table 1. There are two peaks assigned to $Cu_{2p_{3/2}}$ (932.5 eV) and $Cu_{2p_{1/2}}$ (952.5 eV) in the Cu_{2p} region for catalyst **a**. On the other hand, four peaks were observed for catalyst **b** (933.7 and 945.9 eV for $Cu_{2p_{3/2}}$, 953.7 eV and 965.1 eV for $Cu_{2p_{1/2}}$). The former chemical shifts suggest that copper existing on the surface of catalyst **a** is either Cu_2O or CuO [13]. With respect to the discrimination between Cu_2O and CuO for catalyst **a**, the chemical shift of the Cu_{LVV} peak (569.0 eV) is quite close to that of Cu_2O [13], and the other peak corresponding to CuO was below the detection limit. Hence, copper species existing near the surface of catalysts **a** and **b** are considered to be Cu_2O and CuO, respectively; this form of oxide is also supported by the fact that only oxygen was detected as potential counter-anion species. As for zinc on catalysts **a** and **b**, two peaks in the Zn_{2p} region and one peak in the Zn_{LMM} region were commonly detected (table 1). Therefore, zinc is in the same oxidation state for both catalysts, and all the peaks are assignable to Zn^{2+} in ZnO [13].

Fig. 3 illustrates a part of the XRD spectrum for catalyst **a**. In contrast to the XPS analysis (lacking of metallic Cu), the XRD pattern showed the formation of crystalline (metallic) Cu (19.42° 2θ and 22.48° 2θ), which is accompanied by a very small peak of Cu_2O (16.40° 2θ). With respect to catalyst **b**, the XRD peaks at 15.98° 2θ and 17.38° 2θ confirmed that crystalline CuO was exclusively present on

Table 1
Chemical shifts in XPS spectra for catalysts **a** and **b**

Catalyst	Chemical shift (eV)					
	$Cu_{2p_{3/2}}$	$Cu_{2p_{1/2}}$	Cu_{LVV}	$Zn_{2p_{3/2}}$	$Zn_{2p_{1/2}}$	Zn_{LMM}
a	952.5	932.5	569.0	1022.2	1045.3	498.5
b	953.7, 965.1	933.7, 945.9	568.6	1022.2	1045.2	498.2

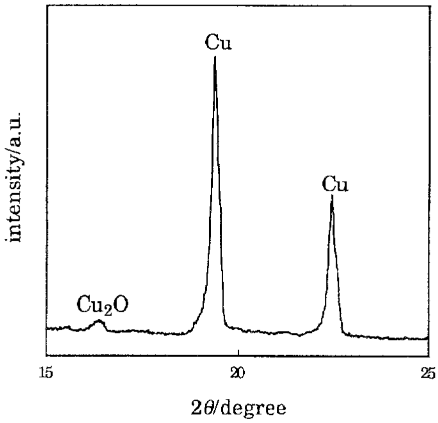


Fig. 3. XRD spectrum of catalyst **a**.

it. The metal species observed by XPS and XRD are tabulated in table 2, and may be taken to indicate the following. (i) Although metallic Cu is mainly found on catalyst **a** (XRD), its surface should be covered with Cu_2O-like species (XPS); its thickness would, however, be several layers. Only XPS signals of CuO_2 are thus detectable, and the XRD of underlying crystalline Cu is not so disturbed. (ii) The form of copper on catalyst **b** is CuO (XRD, XPS). Hence, it can be said that the calcination under N_2 atmosphere resulted in the reduction of Cu(II) to form Cu_2O/Cu, in contrast to the CuO formation by the calcination under dry atmosphere. A possible reductant would be acetyl groups in $Cu(OCOCH_3)_2 \cdot H_2O$.

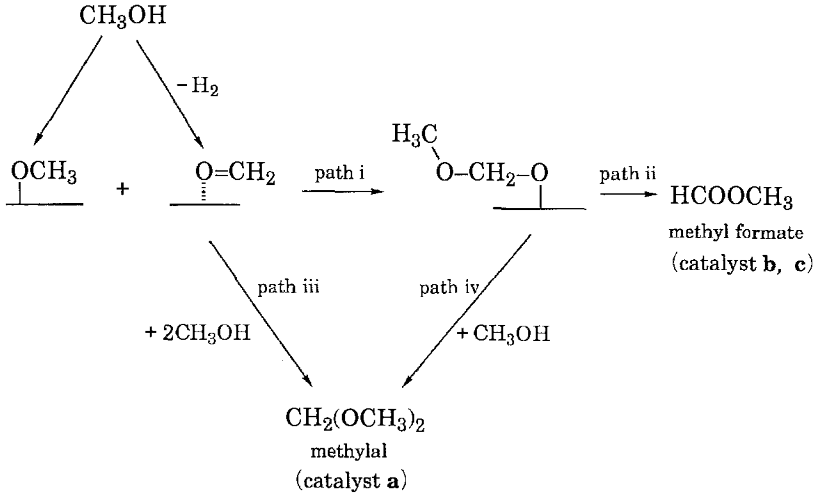
3.4. CONSIDERATION ON THE RELATION BETWEEN THE SURFACE COMPONENT AND THE PRODUCT SELECTIVITY

A feasible mechanism proposed for the formation of methyl formate in the gas–solid phase catalysis is depicted in scheme 1 [14–16], where methyl formate is formed by the reaction between surface methoxy species and adsorbed formaldehyde via a hemiacetal-like intermediate (paths i and ii). It seems reasonable to consider that a similar mechanism is operative for the methyl formate formation here.

With regard to the formation of methylal with catalyst **a** in the liquid-phase

Table 2
XPS and XRD characterization for catalysts **a** and **b**

Catalyst	XPS	XRD
a	Cu(I), Zn(II)	Cu
b	Cu(II), Zn(II)	CuO



Scheme 1.

reaction, the following explanation seems to be possible. The adsorption of methoxy species is considered to be weaker on Cu(I) (catalyst **a**) than on Cu(II) (catalyst **b**). For instance, in the electrochemical reduction of CO_2, methane is formed with CuO electrode (on which methoxy species would be adsorbed strongly enough to be reduced further), while methanol is liberated into the liquid phase as a main product by use of Cu_2O electrode [17]. In addition, when methanol is contacted with Cu–Zn/SiO_2, a larger amount of methoxy species is formed on more oxidized surface [18]. The same character is expected for formaldehyde, which would be bound to acidic sites (Cu(I) and Cu(II)) via oxygen lone-pair electrons (like methoxy species) [19–22]. Thus, the bimolecular reaction to form methyl formate (path i) is disadvantageous on catalyst **a**, because the concentrations of both methoxy species and adsorbed formaldehyde are expected to be relatively small. It would further be anticipated that because of the weak adsorption of formaldehyde, it tends to be liberated into the liquid phase easily, and is then converted to methylal by methanol (path iii), which is present far abundantly compared to the case of gas–solid phase reaction. However, an alternative explanation by the difference in the reactivity of hemiacetal-like intermediate (path iv versus ii) could not be ruled out.

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